ANALYTICAL
ABSTRACTS

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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

1218. The complexones and their analytical application. G. Schwarzenbach (Techn. Hochschule, Zürich, Switzerland). *Analyst*, 1955, **80**, 713–729.—This is a lecture given before the Society for Analytical Chemistry on the theory and practice of compleximetric analysis. N. E.

1219. Use of complexones in analytical chemistry. K. B. Yatsimirskiĭ. *Zavod. Lab.*, 1955, **21** (10), 1149–1157; (11), 1275–1283.—A review with 181 references is given. G. S. SMITH

1220. Significance of steric factors in application of organic compounds as analytical reagents. I. S. Mustafin, T. I. Badayeva and L. M. Kul'berg (Saratov State Univ.). *Ukr. Khim. Zh.*, 1955, **21** (3), 381–383.—Although the sensitivity of benzidine as a colour reagent for CrO_4'' is one-sixth of that of its NN'-tetra-methyl or -ethyl derivatives, that of o-tolidine is 4 times greater than that of its tetramethyl derivative. Similarly, crystal violet is 5 to 8 times more sensitive a reagent for Zn, Cd and Sb than is its $3:3':3''$-trimethyl derivative. The minimum concn. of Mg detectable by azo dyes of the series p-$NO_2 \cdot C_6H_4 \cdot N:N \cdot R$ are as follows—where $R = 2:4$-$C_6H_3(OH)_2$, 5 μg per ml; $R = 3:4$-$C_6H_3 \cdot CH_3 \cdot OH$, 9 μg per ml; $R = 2:4$-$C_6H_3 \cdot CH_3 \cdot OH$, 10 μg per ml; and $R = 2:4:5$-$C_6H_2 \cdot CH_3(OH)_2$, 120 μg per ml. These examples suggest that steric hindrance factors should be taken into account in searching for new reagents. R. TRUSCOE

1221. Studies on oxine and its derivatives: the selectivity and sensitivity of 7-allyl-8-hydroxyquinoline (7-allyloxine) and 7-allyl-8-hydroxy-5-nitrosoquinoline (7-allyl-5-nitroso-oxine) towards certain metals. R. G. W. Hollingshead (British Drug Houses Ltd., Poole, Dorset). *Analyst*, 1955, **80**, 729–735.—In an attempt to increase the selectivity of oxine reagents, 7-allyloxine and 7-allyl-5-nitroso-oxine were prepared and their reactions with Cu, Mg, Ni, Zn and Al examined. It was found that the introduction of an allyl group in the oxine structure does not cause any increase in selectivity, which follows closely that of the parent substance. No increase in selectivity is obtained on the introduction of a nitroso group into the allyl compound in position 5, although an increase in sensitivity occurs. A possible explanation of the non-selectivity of these derivatives is discussed. A. O. JONES

1222. Alumocresone, an improved reagent of the aluminon type. L. M. Kul'berg and L. A. Molot (Saratov State Univ.). *Ukr. Khim. Zh.*, 1955, **21** (2), 256–260.—Condensation of 3-methylsalicylic acid with formaldehyde in H_2SO_4 - HNO_3 gives trimethylaurinetricarboxylic acid (**I**), termed alumocresone, which gives colour reactions with the same ions as does aluminon, but of greater intensity, permitting of their detection in the following minimum amounts (μg) and concn. (p.p.m.): $Fe^{\cdots}$ 0·002 and 0·06, Al 0·007 and 0·2, Be 0·008 and 2·5, $Ga^{\cdots}$ 0·065 and 12·5, $UO_2^{\cdots}$ 0·050, and $PtCl_6''$ 1·3 and 250. The reagent also serves for the colorimetric determination of these ions, in the same way as aluminon. R. TRUSCOE

1223. The use of perfluorocarboxylic acids as separating agents. G. F. Mills and H. B. Whetsel (Carbide and Carbon Chem. Co., Oak Ridge, Tennessee, U.S.A.). *J. Amer. Chem. Soc.*, 1955, **77**, 4690.—Cations are extracted into ether from aq. solutions. The extraction depends on (a) the pH of the aq. layer, (b) the ionic charge on the cation and (c) the nature of the anions present. Perfluorobutyric acid will extract tervalent cations, and $UO_2^{\cdots}$ and $Be^{\cdots}$ can be separated from univalent and other bivalent cations. Perfluoro-octanoic acid will extract bivalent cations. Extraction is best carried out at a pH just less than that necessary to precipitate the cation as an insoluble hydroxide. Analysis of a crystalline product obtained by evaporating the ether extract showed it to be $Fe(OH) \cdot (C_3F_7COO)_2$. Separation factors for individual extractable species vary from 4 to 400 in aq. solutions as nitrate or perchlorate. Fluoride and sulphate prevent extraction. Univalent ions are not extracted, but some, e.g., bismuthyl, can be quant. precipitated by perfluoroacetic acid at pH 0·5. C. A. SLATER

1224. Use of adsorption reactions in qualitative analysis. L. M. Kul'berg and I. N. Bulankhe. *Uch. Zap. Saratovsk. Univ.*, 1954, **34**, 154–175; *Referativnyĭ Zh., Khim.*, 1955, Abstr. No. 14,141.—When a halide is added to a colloidal solution of a silver halide with an adsorbed dyestuff, it displaces the dyestuff, which goes into solution with a change of colour. If a second dye which is not capable of adsorption on the colloidal particles is introduced into the reagent, the sensitivity of the reaction for halides can be increased. Over 40 dyestuffs have been studied. A highly specific method of detecting traces of I' in the presence of very large amounts of Cl' and Br', and a method of detecting Br', Cl' and SCN' are given. Pseudo-adsorption reactions for SO_4'' and F' and adsorption reactions for HPO_4'', WO_4', MoO_4', benzoate and p-chlorobenzoate are described. G. S. SMITH

1225. Qualitative analysis of cations without the use of hydrogen sulphide. S. Ya. Shnaĭderman. *Izv. Kievsk. Politekhn. Inst.*, 1954, **14**, 140–151; *Referativnyĭ Zh., Khim.*, 1955, Abstr. No. 14,143.—The cations are divided into five groups on the basis of the solubilities of the chlorides, sulphates, basic salts, hydroxides and ammonia complexes.

Group I—Ag·, Pb··, Hg^I, Ba·· and Sr···; group reagent—a mixture of $(NH_4)_2SO_4$ and HCl. Group II—Bi···, Sn^{II}, Sn^{IV}, Sb^{III} and Sb^V; group reagent—water, by diluting the solution and heating. Group III—Fe^{II}, Fe^{III}, Al··· and Cr^{III}; group reagent—aq. NH$_3$. Group IV—Co··, Ni··, Cu··, Cd··, Hg^{II}, Mn·· and Mg··; group reagent—NaOH solution after dissolution in excess of aq. NH$_3$ and NH$_4$Cl. Group V—NH$_4$·, K·, Na·, Ca·· and Zn··; no group reagent. Cations within a group are detected in most cases by fractional reactions.   G. S. SMITH

1226. Replacement of hydrogen sulphide and ammonium sulphide in [inorganic] qualitative analysis by organic sulphides. H. Bloemendal and T. A. Veerkamp (Lab. Chem. Embryologie, Amsterdam). *Chem. Weekbl.*, 1955, **51** (53), 943–945.—Criticisms by Bon (*Anal. Abstr.*, 1956, **3**, 324) of the authors' paper on the use of thioacetamide in place of H$_2$S or $(NH_4)_2$S (*cf. Chem. Weekbl.*, 1953, **49**, 147) are answered in detail.   P. S. ARUP

1227. The use of lithium hydroxide for the qualitative separation of the copper and arsenic groups. C. F. James and P. Woodward (The University, Bristol, England). *Analyst*, 1955, **80**, 825–827.—The alleged superiority of LiOH over NaOH and KOH for the efficient qual. separation of the Cu and As groups (Holness *et al.*, *Brit. Abstr. C*, 1950, 470) has been investigated. The most satisfactory reagent for separation of the individual sulphides of group 2B from those of group 2A is 0·5 N KOH, but difficulties may arise with certain combinations of ions. In the presence of ions from group 2B, HgS may dissolve in alkali sulphides and appear in that sub-group. Bivalent Sn should preferably be oxidised before pptn. Acidification of the alkaline soln. of group 2B sulphides causes loss of H$_2$S, and, for quant. re-pptn., H$_2$S should be passed into the soln. Inclusion of KNO$_3$ with LiOH to prevent colloidal dispersion of the ppt. is unnecessary if pptn. is made from a hot soln. and the rate of admission of H$_2$S is suitably controlled. The use of LiOH appears to have no advantage over KOH in equiv. concn. and 0·5 N KOH has the advantage of being able to dissolve SnS$_2$.   A. O. JONES

1228. Use of surface-active substances for preventing co-precipitation of ions with sulphide precipitates. N. A. Rudnev (V. I. Vernadskii Inst. Geochem. and Anal. Chem. Acad. Sci. USSR, Moscow). *Zh. Anal. Khim.*, 1955, **10** (4), 217–221.—Materials capable of reducing the amount of co-pptn. of Tl with As$_2$S$_3$ are studied. The most effective are brilliant green, neutral red and malachite green. Saponin, starch, tannin and gelatin are much less effective, or valueless.

G. S. SMITH

1229. The thermal stability of analytical standards. II. C. Duval, C. Wadier and Y. Servigne (Lab. Recherches Micro-analytiques, Paris). *Anal. Chim. Acta*, 1955, **13** (5), 427–430.—Thermogravimetric curves and i.r. absorption spectra are reported for cryst. citric acid, ammonium acetate, BaCO$_3$, Ba(OH)$_2$, Ba(NO$_3$)$_2$, H$_3$BO$_3$, NH$_4$Cl, As$_2$O$_3$, CdSO$_4$.2·67H$_2$O, (NH$_4$)$_3$HPO$_4$, Al$_2$(SO$_4$)$_3$.K$_2$SO$_4$.24H$_2$O and Na$_2$WO$_4$.2H$_2$O, all of which are used in the preparation of standard solutions for titrimetry (*cf. Anal. Abstr.*, 1955, **2**, 3272).   W. J. BAKER

1230. Influence of organic solvents on adsorption-indicator processes. J. Bognár and S. Sárosi (M. Rákosi Tech. Univ. Heavy Industry, Miskolc, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1955, **7** (3–4), 361–371.—This is an English version of the paper published in *Magyar Kém. Foly.*, 1955, **61** (5), 149. (See *Anal. Abstr.*, 1956, **3**, 7).

1231. Sodium metavanadate as volumetric reagent. IV. Iodine monochloride method. Balwant Singh and Sarwan Singh (Punjab Univ. Coll., Hoshiarpur, India). *Anal. Chim. Acta*, 1955, **13** (5), 405–408.—Sodium metavanadate can be used for the volumetric determination of bivalent Cu, Zn, Co, Hg and Pb in HCl soln. (7 to 7·5 N); Cu··, Zn·· and Co·· are pptd. as complex mercury thiocyanates, Hg·· as mercuric zinc thiocyanate, and Pb·· as PbI$_2$. The thiocyanates are dissolved in conc. HCl (25 to 30 ml) and titrated against 0·1 N NaVO$_3$ in the presence of 0·02 N ICl (5 ml) as pre-oxidiser and catalyst. The addition of ICl is unnecessary when titrating PbI$_2$ (dissolved in HCl) against NaVO$_3$. Chloroform (5 ml) is used as indicator, the colour change during titration being from pink to pale yellow. The error is almost negligible.   W. J. BAKER

1232. Sensitivity of bromine - bromide potentiometric end-point. W. C. Purdy, E. A. Burns and L. B. Rogers (Massachusetts Inst. Techn., Cambridge, Mass., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1988–1994.—Factors influencing the value of the reagent blank in bromine - bromide potentiometric end-points have been studied experimentally and the results are discussed in detail. The size of the blank can decrease with increased surface-area of the indicator electrode, with increased rate of stirring of the soln., or with decreased potentiometer current (*i.e.*, polarisation). The value of the blank also depends on the concn. of reagents, material of electrode, and electrode pretreatment. By careful control of the experimental conditions it is possible to reduce the size of the potentiometric blank until it is approx. equiv. to the corresponding amperometric blank, the sensitivities for the two methods being then the same, when identical electrodes are used. A comparison is made of the two end-points for coulometric determinations of 77 and 7·7 μg, respectively, of As.   W. J. BAKER

1233. Application of ion exchangers in analytical chemistry. V. Elution constants of last traces. D. Jentzsch (Forschungsinst. NE-Metalle, Freiberg, Saxony, Germany). *Z. anal. Chem.*, 1955, **148** (5), 321–324.—The elution constants for last traces (*cf. Anal. Abstr.*, 1956, **3**, 332) of Al, As, Ca, Co, Mg, Ni, Fe, Cd, Cu, Mn and Zn eluted with HCl from Wofatit L 150 are plotted. These constants permit the more accurate calculation (illustrated by examples) of the separation of the different elements or groups of elements. Cobalt is strongly adsorbed and cannot be quant. separated from Cd; similarly the separation of Ni and As^{III} in > 7 M acid should not be attempted.

VI. Dependence of elution constants on the concentration of an element. D. Jentzsch. *Ibid.*, 1955, **148** (5), 325–333.—The dependence of the elution constants E_s and E_1 on concn. for Zn, Cd and Cu is determined and plotted. These measurements permit the prediction of favourable experimental conditions for concn. differing from those commonly used. The adsorption of the elements

depends on the extent of complex formation and on pure physical adsorption; the variation of the elution constant E_a with acid concn. and with the concn. of the element affords an indication of the behaviour of the complex on the exchanger. The E_a values of all three elements are least dependent on concn. in the region of strongest adsorption; the more highly charged the complex, the more firmly is it bound at high acid concn. Thus the observed increase in E_a of different elements with increasing acid concn. may be ascribed to the formation of multi-charged complexes.

J. P. STERN

1234. **Behaviour of ultramicro amounts of elements. I.** A. K. Lavrukhina (V. I. Vernadskiĭ Inst. Geochem. and Anal. Chem. Acad. Sci. SSSR, Moscow). *Zh. Anal. Khim.*, 1955, **10** (4), 203–210. —An account is given of the co-pptn. of radio-isotopes, mainly with hydroxides and sulphides of various metals. G. S. SMITH

2.—INORGANIC ANALYSIS

1235. **Development of polarographic analysis of inorganic substances. (Review of work 1952–1954.)** I. V. Pyatnitskiĭ. *Zavod. Lab.*, 1955, **21** (7), 798–807.—A review of work carried out in Russia and other countries is given. (79 references.) G. S. SMITH

1236. **Potentiometric method for determining a number of metals (Pb, Cu, Zn, Ni, Cd, Sn and Mg) by means of EDTA (disodium salt).** L. M. Budanova and O. P. Platonova. *Zavod. Lab.*, 1955, **21** (11), 1294–1300.—Examples of direct potentiometric titrations of various metals in ammoniacal solution with EDTA (disodium salt) (**I**), and of back-titrations of the excess of **I** with lead nitrate solution are given. G. S. SMITH

1237. **The analysis of inorganic compounds by paper chromatography. VII. A multiple-spot phenomenon.** F. H. Pollard, J. F. W. McOmie, J. V. Martin and C. J. Hardy (University Bristol, England). *J. Chem. Soc.*, 1955, 4332–4337.— The investigation reported shows that the R_F value of a metal on a chromatogram depends on the anion of the salt used and on the anion(s) or complex-forming agent in the eluting solvent. With certain combinations of these factors, multiple spots can be obtained. The behaviour of the strontium cation initially present as chloride, nitrate or acetate with a mobile phase of aq. *n*-butanol containing acetic acid is described. For quant. analysis, a compact spot is produced in the absence of a complex-forming agent by starting with salts in which the anion corresponds to the anion of any acid or salt contained in the eluting solvent, or in the presence of a complex-forming agent by keeping the acidity sufficiently low and the concn. of the complex-forming agent sufficiently high to ensure that the metal finally forms a single spot of the complex.

VIII. The separation of the thionic acids by a new paper-chromatographic technique. F. H. Pollard, J. F. W. McOmie and D. J. Jones. *Ibid.*, 1955, 4337–4340.—The effect of a phase boundary on the separation of the thionic acids by the use of an organic solvent containing K acetate is discussed, with particular reference to the problem

of double-zoning and the formation of two mobile phase-regions on the chromatogram. A new technique is described, which eliminates this double-zoning, whereby the substances to be separated are placed on the paper after the phase boundary has passed the starting line. A solvent system is suggested for the complete separation of the potassium salts of the thionic acids by means of this technique. O. M. WHITTON

1238. **The chromatographic separation of different elements in different valency states.** F. H. Pollard, J. F. W. McOmie and A. J. Banister (Univ. Bristol, England). *Chem. & Ind.*, 1955, (49), 1598.—With the eluting mixture given, about 25 μg of each compound may be separated in as little as 1 hr. on acid-washed Whatman No. 1 filter-paper by ascending chromatography. The preferred solvent mixture consists of conc. HCl - H₂O - ether - methanol (4 : 15 : 50 : 30), mixed in the order given. Results are given for Cu, As, Sb, Cr, Mo [located with (dithiol + thioglycollic acid) in methanol], and Co [with the solvent system conc. HCl - H₂O - ether - methanol (2 : 20 : 50 : 30)]. With some modifications, similar solvent systems can be successfully used for separating Hg^I and Hg^{II} (ether - methanol - aq. HNO_3); Pt^{II} and Pt^{IV} (ether - methanol - H₂O); and V^{IV} and V^V (ether - methanol - aq. acetic acid). The same (or slightly modified) solvent systems can also be used in ascending or descending chromatography for separating the following mixtures—LiCl, NaCl, NH₄Cl and KCl; NH₄Cl, N₂H₄, NH₂OH, and substituted compounds; BeCl₂, MgCl₂, CaCl₂, SrCl₂ and BaCl₂; aluminium, rare-earth, titanium, iron and uranium chlorides; uranium from other metals; and cobaltammine complexes. O. M. WHITTON

1239. **Paper chromatography of some metal β-diketone chelates.** J. E. Strassner (Louisiana State Univ., U.S.A.). *Dissert. Abstr.*, 1955, **15** (8), 1309.—Nickel, Co and Cu can be separated chromatographically as acetylacetonates on paper by using a mixture of *cyclo*hexane, dioxan and methanol (84 : 10 : 6) as developing solvent. By means of the perfluorobutyryl-2-thenoylmethane chelates, Fe, Cu, Ni, Co and Mn can be separated with a mixture of light petroleum and methanol (92 : 8); replacement of 1 part of methanol in the solvent by dioxan allows separation of the 2-furoylperfluorobutyrylmethane chelates. A qual. relation was found between the R_F values and solubilities and relative adsorption affinities. The potentialities of the thenoyl- and furoyl-perfluorobutyrylmethane chelating agents as spot-test reagents are surveyed. S. C. JOLLY

1240. **The pH ranges of precipitation of some metal - hydroxyquinoline compounds.** R. Bock and F. Umland (Tech. Hochsch., Hanover, Germany). *Angew. Chem.*, 1955, **67** (16), 420–423.— The relation between oxine precipitation and pH was investigated for various metals and the necessity of establishing the pH range for any oxinate precipitation is pointed out. Experiments, carried out under uniform conditions, were designed to analyse the quant. degree and constancy of each precipitation and the stoicheiometric ratio of metal and oxine in the precipitate. Results are arranged according to the groups in the Periodic Table and compared with data from relevant literature.

S.C.I. ABSTR.

1241. Flame spectra of twenty metals using a recording flame spectrophotometer. M. Whisman and B. H. Eccleston (Bur. of Mines, Bartlesville, Okla., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1861–1869.—The paper describes modifications to a Beckman DU spectrophotometer consisting of a photomultiplier phototube in place of the usual phototube and the incorporation of an automatic wavelength drive and recorder; this decreases the time per analysis to about 10 min. and only a small vol. of sample (10 ml) is required. The spectrograms of the following elements are shown together with the tables of the principal lines and an estimated detection limit for each—Ba, B, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Ni, K, Rb, Ag, Na, Sr, Tl, Ti and V. D. G. HIGGS

1242. Chemical analysis of thin films by X-ray emission spectrography. T. N. Rhodin (E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1857–1861.— X-ray emission spectrography has been applied to the quant. analysis of evaporated metallic films (Fe, Ni and Cr) $\not> 300$ A thick. Comparison of results by this technique with those by the normal colorimetric micro-methods indicates an accuracy of better than ± 2 per cent. Oxide films associated with passivity studies and with surface densities corresponding to 1 to 100×10^{-6} g per sq. cm have also been analysed. Mylar polyester film (2.5×10^{-4} in. thick) was chosen as substrate because of its high strength and its very low X-ray scattering power. The metal film was vaporised on to the substrate under a pressure of 10^{-5} mm of Hg. X-ray data were obtained on a plane crystal spectrograph with tungsten target, operated at 50 kV and 35 mA. A lithium fluoride analysing crystal and a Soller blade-collimator (6 in. long with 0·005-in. spacing) were used, and fixed-angle counting was adhered to throughout, with an argon-filled Geiger tube. The first-order $K\alpha$ lines were measured for all the elements except Mo, for which the $L\alpha$ lines were also measured (*cf.* Noakes, *Bull. A.S.T.M.*, 1954, **157**, 43). D. G. HIGGS

1243. Iodimetric determination of oxidising agents. G. D. Nessonova and D. V. Turkovskaya (Moscow Textile Inst.). *Zavod. Lab.*, 1955, **21** (11), 1302–1304.—In the volumetric determination of Cu, 3·5 equiv. of KI are sufficient for 1 equiv. of Cu; the pH of the solution can vary between 0·3 and 7 and the acid used can be HCl, H_2SO_4 or acetic acid without any effect on the results. In the determination of dichromate, 3 equiv. of KI and 2 equiv. of acid are sufficient for 1 equiv. of chromate, but the reaction is not instantaneous. The liberated iodine can be titrated at once with thiosulphate if 10 equiv. of acid are used. G. S. SMITH

1244. Determination of radioactive hydrogen. W. G. Verly, S. Bricteux-Gregoire, G. Koch and G. Espreux (Lab. Pathol. Gén. et Biochem., Univ. Liège, Belgium). *Bull. Soc. Chim. Belg.*, 1955, **64** (9–10), 491–501.—Hydrogen generated from ^{3}H-labelled compounds is introduced into a 100-ml ionisation chamber, which is then filled to atm. pressure with ordinary H. A p.d. of 300 V is applied across the electrodes and the ionisation current is determined with a vibrating-reed electrometer by the rate-of-drift method. One disintegration per sec. can be detected in a background equivalent to two disintegrations per sec. The standard deviation in the measurement of an activity of >15 disintegrations per sec. is <2 per cent. A. JOBLING

1245. Conductimetric determination of alkali sulphide, hydroxide and carbonate in the presence of each other. R. Domanský (Lab. pre výskum drev, Slovenská akadémia vied, Bratislava, Czechoslovakia). *Chem. Listy*, 1955, **49** (2), 186–190.—The method described, based on pptn. with $0.5 N$ $AgNO_3$, is more accurate than the usual conductimetric neutralisation method, and gives good results, especially for the determination of S″ in the presence of OH′. It is less accurate for the determination of CO_3″. Interference is caused by $Na_2S_2O_3$. G. GLASER

1246. Potentiometric determination of sodium ions by means of a glass electrode. O. Tomíček and R. Pulpán (Karlovy Univ., Prague, Czechoslovakia). *Chem. Listy*, 1955, **49** (4), 497–502.—Conditions for the potentiometric determination of Na· in milligram quantities in a medium of 85 to 95 per cent. aq. ethanol by titration with a soln. of zinc uranyl acetate, with a reference electrode made from Jena 20 or Czech K 35 glass, have been determined. The titration is successful even in the presence of K·, provided their concn. is greater than that of the Na·. G. GLASER

1247. Derivative polarography. Determination of sodium in raw materials, intermediates and by-products of the aluminium-producing industry. R. Splítek (Metals Res. Inst., Panenské Břežany). *Hutn. Listy*, 1955, **10** (11), 643–650.—A derivative polarographic method for the determination of Na is described. The method is based on the study of the dependence of the differential coefficient dI/dE on E (E = p.d., I = polarographic current), and has many advantages over classical polarography. The mathematics of the method are discussed, and circuit diagrams are given. A detailed study of many factors influencing derivative polarography was made and possible sources of error are listed. Though more susceptible to error and less reproducible than orthodox polarography, strict observation of the optimum conditions gives equally good results. The method was tried on a number of impure substances, such as bauxites, cryolites and fluorides, as well as on NaCl, Na_2CO_3 and Na_3PO_4. Lithium salt and hydroxide solutions were used as the "indifferent" electrolyte. An error of ± 3 per cent. was obtained. A. O. JAKUBOVIC

1248. Methods for determining sodium and potassium in boiler availability investigations. Boiler Availability Committee of the Institute of Fuel (18 Devonshire St., London). *J. Inst. Fuel*, 1955, **28**, 550.—Sodium and K are determined by flame photometry (*cf.* Collins and Polkinhorne, *Analyst*, 1952, **77**, 430) after extraction from coal (ashed according to B.S. 1016:1942), grit, boiler deposit, etc., by treatment with HF. Accompanying heavy metals are pptd., or the Na and K are isolated by ion exchange (Logie and Rayner, *J. Inst. Fuel*, 1953, **26**, 146). Wet oxidation of coal, and the Lawrence Smith extraction of alkalis, are satisfactory alternative methods. In boiler deposits, soluble alkali-metal compounds should be determined separately. A. R. PEARSON

1249. Direct determination of moisture in sodium hydroxide. C. L. Dunning and C. D. Hildebrecht (Diamond Alkali Co., Painesville, Ohio, U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1927–1929.—The method

described involves heating the sample (50 to 100 g) at 350° C for 30 min. in a closed nickel cylinder and absorbing the evolved H_2O in two weighed U-tubes filled with solid magnesium perchlorate (anhydrone). The whole operation is effected in a stream of dry nitrogen. A result, accurate to ± 0.012 per cent., can be obtained in $\simeq 45$ min. for samples of NaOH containing from 0.02 to over 1 per cent. of water.

W. J. Baker

1250. The micro-determination of potassium with dipicrylamine. P. R. Lewis (Physiological Lab., Cambridge, England). *Analyst*, 1955, **80**, 768–773. —A method is described for the micro-determination of K in biological material. *Procedure*—The sample (20 to 100 μg of K) is dried and ashed at 550° C or lower. The ash is dissolved in 2 or 3 drops of water and 1 drop of the lithium dipicrylamine reagent (prep. described) is added and followed by second and third drops at 10-min. intervals, and finally by enough to provide a twofold excess of the dipicrylamine ion. The crystalline ppt. is washed with ice-cold water, then dissolved in hot water. The vol. is adjusted so that the soln. contains 30 to 70 μg of K per 100 ml and the extinction is measured in a Spekker absorptiometer with a blue filter (Ilford, No. 601, 602, 621 or 622). The calibration graph is linear. With biological samples the heavy metals likely to interfere are converted into insoluble compounds during the ashing. With a ratio of Na to K of 50 to 1 the error should not exceed 2 per cent. A. O. Jones

1251. Radiometric micro-determination of potassium in the form $K_2Na[Co(NO_2)_6]$. I. M. Korenman, F. R. Sheyanova and Z. I. Glazunova (Sci. Res. Inst. Chem., Gorki State Univ.). *Zavod. Lab.*, 1955, **21** (7), 774–776.—Potassium is determined in the form $K_2Na[Co(NO_2)_6]$ by using radioactive ^{60}Co in the precipitant and determining the activity of the solution of the ppt.; 0.1 mg of K in 0.5 ml can be satisfactorily determined. G. S. Smith

1252. Co-precipitation of caesium with potassium picrate. I. M. Korenman, P. A. Ganichev and V. V. Gorshkov (Gorki State Univ., USSR). *Zh. Anal. Khim.*, 1955, **10** (5), 327–330.—By means of solutions containing ^{134}Cs the co-pptn. of Cs with K from ethanol solutions of picric acid was studied. The co-pptn. has little effect on the determination of K by the picrate method, but the subsequent determination of small amounts of Cs shows a considerable relative error. With ethanol solutions of picric acid, determinations of K should be carried out at 0° C. G. S. Smith

1253. Dithiocarbazic acid as a specific reagent for copper. A. G. Kovaleva. *Uch. Zap. Saratovsk. Univ.*, 1954, **34**, 176–179; *Referativnyǐ Zh., Khim.*, 1955, Abstr. No. 14,197.—Dithiocarbazic acid at pH 3 to 9 gives, with most metal ions, characteristic coloured ppt. insol. in water and organic solvents. Copper salts give a black ppt. containing CuS, Cu_2S and NH_2NHCS_2Cu. To detect Cu, a drop of the solution is placed on filter-paper which has been treated with zinc or cadmium nitrate solution (10 mg per ml), then dried and immersed in a 1 per cent. aq. solution of the reagent; 0.2 μg of Cu can be detected at a dilution of 1 in 20,000. The test is applicable in the presence of salts of metals of all five analytical groups together with the rare and rare-earth metals (46 have been tested). To detect Cu in alloys and minerals, 2 to 10 mg are dissolved in HCl or H_2SO_4, and if necessary HNO_3, and

$Na_4P_2O_7$ or NaF is added if the iron content is high The solution is diluted with water and a drop of the filtered solution is placed on the prepared filter-paper. A black coloration in the centre of the spot indicates Cu. The test can be carried out also on the surface of an alloy (steel, nickel, duralumin) or mineral. G. S. Smith

1254. Colorimetric determination of copper by means of ethanolamine. I. P. Ryazanov and N. I. Davydova. *Uch. Zap. Saratovsk. Univ.*, 1954, **34**, 194–199; *Referativnyǐ Zh., Khim.*, 1955, Abstr. No. 14,198.—Ethanolamine gives with Cu'' a lilac - blue solution, the colour of which remains const. for 5 to 6 hr. and obeys Beer's law over the concn. range 300 to 540 μg of Cu per ml. With 2 N ethanolamine, 19.5 μg of Cu can be detected in 1 ml of solution (dilution 1 in 50,000); it can be determined by means of a series of standards or by colorimetric titration. To determine Cu in lead - antimony alloys, 5 g are dissolved in 30 ml of dil. HNO_3 $(1 + 4)$, 3 to 4 ml of dil. H_2SO_4 $(1 + 1)$ are added, and the $PbSO_4$ is filtered off after 30 min. and washed with cold 2 per cent. H_2SO_4. The filtrate is evaporated just to dryness and the residue is dissolved in water. At the same time a comparison solution is prepared from dil. H_2SO_4. To each solution 5 ml of 2 N ethanolamine are added and the Cu in the sample is determined by colorimetric titration. The method is preferred to the pyridine - thiocyanate method. G. S. Smith

1255. Photometric determination of copper in molybdenum products with benzoin α-oxime. J. Madera (Climax Molybdenum Co., Langeloth, Pa., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 2003–2004.— From 0.001 to 1.00 per cent. of copper in molybdenum metal, molybdenite concentrates, purified MoS_2, MoO_3, molybdenum silicide, etc., can be accurately determined by the benzoin α-oxime method of Dunleavy (*Brit. Abstr. C*, 1950, 265), the extinction of the $CHCl_3$ extract of the complex being measured at 440 mμ in 1-cm cells (slit width 0.065 mm). Procedures for dissolving a wide variety of molybdenum products and then developing the colour at pH 11.3 to 12.3 are given. The method is more sensitive than is the gravimetric thiocyanate - electrolytic procedure, but ratios of Ca : Cu > 2 (as in calcium molybdate samples) cause appreciable interference. W. J. Baker

1256. Copper salicylaldoxime and its use in the heterometric micro-determination of copper in the presence of foreign metals. M. Bobtelsky and E. Jungreis (Hebrew Univ., Jerusalem, Israel). *Anal. Chim. Acta*, 1955, **13** (5), 449–454.—By using the apparatus and procedure described previously (11 references cited), a method for the heterometric determination of copper with salicylaldoxime at 20° C has been developed. Initial pptn. of Cu salicylaldoximate occurs at pH $\simeq 1.5$ and is complete only in the pH range 3 to 10, beyond which the ppt. redissolves to a clear soln. In 10 ml of 0.1 M acetic acid, 1 mg of Cu in $\simeq 99$ per cent. of other bivalent metals, or $\simeq 90$ per cent. of tervalent metals, can be titrated heterometrically to within ± 1 to 2 per cent., with 0.2 M sodium citrate or tartrate as masking agent for Al or Cr (95 per cent. concn.), or with citrate if $\simeq 95$ per cent. of Fe is present. A titration takes from 15 to 20 min.; a blue or green filter (but a red one for iron) is used. Copper is not pptd. at any pH in the presence of EDTA. W. J. Baker

1257. Analysis of bronze by means of a cationite.
V. I. Lenskaya and L. I. Pen'kova. *Uch. Zap.
Saratovsk. Univ.*, 1954, **34**, 185–188; *Referativnyĭ
Zh., Khim.*, 1955, Abstr. No. 14,268.—Bronze (1 g)
is dissolved in 15 to 20 ml of dil. HNO_3 (1 + 1), the
solution is evaporated to a vol. of 5 to 10 ml; 100 ml
of hot water and 20 ml of 15 per cent. ammonium
nitrate solution are added and the solution is boiled
and set aside in a hot place. The metastannic acid
is filtered off and washed with hot dil. HNO_3 (3
per cent.) and the filtrate is diluted to 200 ml in a
calibrated flask. A 20-ml aliquot of the solution
is made just alkaline with N NaOH and then just
acid with 2 per cent. aq. HNO_3, and passed through
a sulphophenol ammonium cationite filter at the
rate of 5 to 6 drops a min. Aluminium, Cu and Fe
are adsorbed. The Al is extracted by washing the
filter with 80 ml of 5 per cent. aq. NaOH at the
rate of 8 to 10 ml per min., followed by 100 to 120
ml of water, and is determined colorimetrically or
gravimetrically. To extract the Cu and Fe, the
cationite is washed with hot 5 per cent. HCl solution
into a receiver containing 20 to 30 ml of conc.
aq. NH_3. The ppt. of $Fe(OH)_3$ is collected and
dissolved in HCl and the Fe is determined colori-
metrically as thiocyanate. The Cu is determined
by electrolysis of the ammoniacal solution.
　　　　　　　　　　　　　　　　　G. S. SMITH

**1258. Determination of silver in production
control of light-sensitive photographic materials.**
L. M. Kul'berg and A. Ya. Roĭtman. *Uch. Zap.
Saratovsk. Univ.*, 1954, **34**, 142–153; *Referativnyĭ
Zh., Khim.*, 1955, Abstr. No. 14,203.—Silver halide
from the material to be analysed is brought into
solution by treatment with a mixture of H_2SO_4
and HNO_3, either directly or after preliminary
reduction, and $Ag^{\cdot}$ are titrated with iodine in KI
solution, in the presence of starch. The method is
applicable to the analysis of photo-emulsions, pptd.
photo-emulsions, emulsion washings, ashes of waste
photo-paper and photo-materials prepared for use.
　　　　　　　　　　　　　　　　　G. S. SMITH

**1259. Amperometric study of the precipitation
reactions of heavy-metal ferrocyanides. II. Pre-
cipitation of silver ferrocyanide.** G. A. Kleĭbs
(Kuibishev Aviation Inst.). *Zh. Anal. Khim.*,
1955, **10** (4), 244–250.—The addition of 0·1 M
$K_4Fe(CN)_6$ to 0·1 M $AgNO_3$ containing KNO_3 or
$NaNO_3$ first precipitates $Ag_4Fe(CN)_6$, which reacts
with ions in solution to give $KAg_3Fe(CN)_6$. Con-
versely, but in the absence of KNO_3, the double
compound is converted into the normal compound
when there is an excess of $Ag^{\cdot}$ present.
　　　　　　　　　　　　　　　　　G. S. SMITH

**1260. Detection and colorimetric determination of
gold with ascorbic acid.** S. Ya. Shnaĭderman
(Kiev Polytech. Inst., Ukrain. SSR). *Ukr. Khim.
Zh.*, 1955, **21** (2), 261–264.—To 10 ml of solution
(pH 3 to 6), containing 10 to 100 μg of Au^{III}, are
added 1 ml of 1 per cent. ascorbic acid solution,
a drop of 0·5 per cent. starch solution, and water to
25 ml. The extinction is measured after 5 min.,
and the content of Au is read from an empirical
curve; the coloration is stable for at least 1 hr.
In the absence of other ions, the colour reaction
serves for the detection of $\ngtr$0·1 p.p.m. of Au^{III},
and of $\ngtr$6·6 × 10^{-5} M Au^{III} in the presence of a
20-fold excess of Fe, Mn, Ni, Co, Cu, Sb, Pb,
Zr, $UO_2^{\cdot\cdot}$ and rare-earth-metal nitrates, sulphates
and chlorides, or of $NaVO_3$, $(NH_4)_2WO_4$,
$(NH_4)_2MoO_4$, K_2Se or K_2Ta; salts of Ag interfere.
　　　　　　　　　　　　　　　　　R. TRUSCOE

**1261. The Tananaev method in the assay of gold
and platinum alloys.** V. Šilhanová and J. Kvaček
(Výzkumná lab. puncovní služby, Prague, Czecho-
slovakia). *Chem. Listy*, 1955, **49** (2), 266–268.—
Preparation of the sample—Treat the surface of the
noble metal to be assayed with a drop of aqua regia
and evaporate to dryness (repeatedly if necessary)
until sufficient residue for the spot-test is obtained.
Dissolve the residue in a drop of water, transfer the
soln. by means of a capillary tube to a watch-glass,
evaporate to dryness with HCl, and redissolve the
residue in water. Any Ag present remains undis-
solved as AgCl. *Detection of Au*—Gold is detected
by the immediate formation of a blue spot when a
drop of the test soln. is placed on filter-paper im-
pregnated with a soln. of benzidine; $Ir^{\cdots\cdot}$ interfere.
Alternatively, a soln. of a ferrous salt, with which
Au develops a black colour, can be used as impreg-
nating soln. In the presence of Pd, the reagent
used is a soln. of dimethylglyoxime; Pd remains as
a yellow ppt. in the centre, whilst Au is found on the
circumference of the spot, where its presence is
detected by means of $SnCl_2$. *Detection of Pt*—In
the absence of Pd and Au, Pt is best detected by the
formation of a yellow or orange stain with $SnCl_2$.
In the presence of a little Au and Pd, the detection
of Pt is based on the formation of a yellow ppt. of
Tl_2PtCl_6 with $TlNO_3$. In solutions free from $Ir^{\cdots\cdot}$
and $Au^{\cdots}$, Pt can be detected by the formation of a
blue spot with benzidine. *Detection of Pd*—One
method is based on the formation of a dark-brown
complex of $Tl_2AuPdCl_7$ when $Tl^{\cdot}$ react with $Pd^{\cdot\cdot}$
and $Au^{\cdots}$. A drop of a soln. of $Au^{\cdots}$ is placed on
paper impregnated with aq. $TlNO_3$, followed by a
drop of the test soln. In a second method for
detecting Pd, the formation of a yellow complex
between Pd and thiourea is used. *Detection of Ir*—
The best procedure is based on the immediate
formation of a blue coloration with benzidine.
Interference by $Au^{\cdots}$ must be eliminated by reduc-
tion with $Fe^{\cdot\cdot}$, followed by re-oxidation of $Ir^{\cdots}$
to $Ir^{\cdots\cdot}$ by means of HNO_3. Alternatively, Ir can
be detected by changing the yellow colour produced
by treating aq. NH_4Cl soln. with $Pt^{\cdots\cdot}$ to orange.
Detection of Rh—Rhodium forms a cherry-red
coloration on reduction with $SnCl_2$ in the presence
of NH_4Cl and KI. The reagent is prepared by
mixing 2 ml of saturated aq. NH_4Cl soln. with 1 ml
of saturated aq. KI soln. and 1 ml of 20 per cent.
$SnCl_2$. Gold, Pt and Pd must be removed by
treating the sample on a watch-glass with a drop
of ethanol, a crystal of dimethylglyoxime, a drop
of a saturated soln. of Mohr's salt and a few crystals
of NH_4Cl; the supernatant soln. is then used for
the test.　　　　　　　　　　　　　G. GLASER

**1262. Separation of group IIA elements of the
periodic table by paper chromatography.** R. J.
Magee and J. B. Headridge (The University,
Edinburgh). *Analyst*, 1955, **80**, 785–788.—In the
method described, Be, Mg, Ca, Sr and Ba are
separated by descending paper-chromatography.
Examination of a number of solvent mixtures
resulted in the choice of methanol - n-butanol -
sym.-collidine - 6 N acetic acid (40:20:20:20 per
cent. v/v). The metals in the form of chlorides are
applied to the paper (Whatman No. 3MM filter
strip), which is dried and placed in the chromato-
graphic chamber, and the solvent is allowed to
descend for 45 to 50 cm in 16 to 18 hr. The air-
dried paper is heated over a hot-plate until little
odour of the solvent persists, and is then sprayed
with an alkaline 8-hydroxyquinoline soln., dried and
examined in u.v. light. Calcium, Mg and Be

fluoresce brilliantly and the bands are compared with standards. For the detection of Ba and Sr the upper portion of the paper is sprayed with Na rhodizonate soln. and compared with standards. The group IIA metals, in amounts up to 10 μmoles, do not interfere with the estimation of 0·1 μmole of any particular metal except Ca, of which the minimum amount detectable in the presence of 10 μmoles of Mg is 0·25 μmole.   A. O. JONES

1263. Colour reactions for beryllium. V. I. Kuznetsov (V. I. Vernadskiĭ Inst. Geochem. and Anal. Chem. Acad. Sci. SSSR, Moscow). *Zh. Anal. Khim.*, 1955, **10** (5), 276–285.—Organic reagents for Be are reviewed. The properties of a number of new reagents and their reactions with Be and other metals are described. "Arsenazo" [o-(1:8-dihydroxy-3 : 6-disulpho-2-naphthylazo)benzenearsonic acid] as a colour reagent for Be is studied in detail. In neutral solution a red - violet colour appears (limiting dilution 1 in 100,000,000; minimum amount of Be detectable 0·02 μg). The interference of all other elements that react with the reagent can be masked. To detect Be in minerals, 2 to 5 mg of the powdered material are fused with Na_2CO_3, the melt is dissolved in HCl, and the solution is diluted with water. One or two drops of 60 per cent. aq. stannic chloride solution are added (some of the interfering elements are co-pptd. with the stannic acid formed by hydrolysis), the solution is boiled and made only slightly acid to Congo red with $NaHCO_3$ solution. The solution is filtered, drops of saturated solutions of Na K tartrate and ammonium oxalate are added and then 25 per cent. hexamine solution to neutralise. Similar vol. are taken in two test-tubes. That in one tube is treated with one or two drops of 0·05 per cent. arsenazo solution, that in the other with bromothymol blue solution. Both solutions are then treated with the same no. of drops of saturated borax solution until the tube containing the bromothymol blue shows a deep-green colour. In the presence of Be, the solution containing arsenazo shows a red - violet colour, which remains unchanged on the addition of H_2O_2.   G. S. SMITH

1264. Volumetric determination of beryllium. Hydrolysis of beryllium sulphate by means of a mixture of potassium iodide and iodate. B. Suseela (Hindu Univ., Benares, India). *Zh. Anal. Khim.*, 1955, **10** (5), 286–288.—Beryllium sulphate solution is mixed with an excess of 0·05 M KIO_3, 3 to 5 g of KI and a known vol. of N $Na_2S_2O_3$ in excess in a flask with a ground-glass stopper. The mixture is set aside at 50° to 60° C for 4 to 5 hr., the solution is then cooled and the excess of thiosulphate is determined by titration with iodine solution. The stability of thiosulphate solution under these conditions is confirmed.   G. S. SMITH

1265. Paper chromatography of inorganic ions. XII. The separation of beryllium, germanium, indium and gadolinium. R. G. de Carvalho and M. Lederer (Inst. Radium, Paris). *Anal. Chim. Acta*, 1955, **13** (5), 437–438.—The behaviour of Be··, In····, Ge···· and Ga··· in various mixtures of n-butanol and HCl is discussed, with special reference to the variation of R_F values. An effective separation of these four ions can be made by paper chromatography, with a solvent mixture of n-butanol, conc. HCl and H_2O (10:3:7); the concn. of HCl in this mixture is 3 N.   W. J. BAKER

1266. Determination of "water-soluble calcium" in gypsum. W. A. C. Campen, L. J. H. Nijst and P. J. Neis. *Chem. Weekbl.*, 1955, **51** (53), 945–947. —The determination of the agriculturally important water-soluble salts of Ca in gypsum is considerably facilitated by the use of aq. 1 per cent. sucrose as solvent instead of water; $CaSO_4$ (like CaO) forms a readily sol. complex with sucrose, without alteration in the pH of the soln. The determination of Ca in the filtered soln. is preferably carried out by titration with EDTA (disodium salt), with murexide as indicator. The end-point of the titration is determined as the point at which the transmission of (unfiltered) light from an electric lamp through the soln., as measured by a selenium cell connected with a galvanometer, is reduced to a minimum.   P. S. ARUP

1267. Studies in the simultaneous flame-photometric determination of calcium, barium and strontium. Determination of small amounts of barium in the presence of large amounts of calcium and strontium. E. Pungor and A. Hegedüs (Eötvös Loránd Sci. Univ., Budapest). *Magyar Kém. Foly.*, 1955, **61** (10), 308–312.—In the range 650 to 930 mμ, regions can be chosen in which the interference of Ca and Sr in the determination of Ba is negligible if a narrow slit is used; with a wider slit (0·5 mm) the interference is additive. The error can be calculated by carrying out the determination at two wavelengths (750 and 870 mμ).   A. G. PETO

1268. New photocolorimetric method for determining zinc with thiocyanate and rhodamine C. L. B. Zaĭchikova and N. N. Lutchenko (State Scientific Res. Inst. Non-Ferrous Metals). *Zavod. Lab.*, 1955, **21** (11), 1304–1307.—The colour of the reaction product of Zn with thiocyanate and rhodamine C at pH 5 has a max. absorption at 620 to 660 mμ, which corresponds to the minimum absorption with rhodamine C. The molar absorption coeff. is $\simeq 4{\cdot}6 \times 10^4$. With 50 μg of Zn in 60 ml the colour is stable for 30 min. and with 10 μg in 60 ml for 3 hr.; Fe and Cu interfere, but Fe is rendered harmless by reduction with hydroxylamine, and Cu, up to 1 per cent., by the addition of thiourea. For samples containing less than 1 per cent. of Cu, the sample (0·1 g) is attacked with HCl, followed by HNO_3, and the solution is evaporated with H_2SO_4. The residue is taken up in water and the solution is filtered. A portion of the filtrate in a 50-ml cylinder is treated with 5 ml of 20 per cent. hydroxylamine hydrochloride solution, 5 ml of a buffer solution containing 15 per cent. of sodium acetate and 3 per cent. of acetic acid, 4 ml of freshly prepared 10 per cent. thiourea solution and 5 ml of 20 per cent. KSCN solution. The solution is diluted to 50 ml and exactly 10 ml of 0·02 per cent. rhodamine C solution are added. The extinction of the solution is measured, with a red filter. A blank is carried out at the same time, and the content of Zn is found from a calibration curve. For samples containing more than 1 per cent. of Cu, the solution of the sample obtained as described above is boiled with $Na_2S_2O_3$ solution to ppt. CuS. No thiourea is added and only 2 ml instead of 5 ml of hydroxylamine hydrochloride solution are used. For the determination of Zn in pyrites concentrates, the sample is attacked with HCl alone.   G. S. SMITH

1269. Determination of small amounts of zinc in aluminium alloys. D. V. Romanov. *Zavod. Lab.*, 1955, **21** (7), 782–785.—The addition of $Na_4P_2O_7$

solution, followed by aq. NH$_3$, to a solution containing Al, Fe, Mn, Cr, Zn, Cu and Ni gives complex anions of Al, Fe, Mn and Cr of the type [M(P$_2$O$_7$)$_3$]$'''''''$ or [M(P$_2$O$_7$)$_3$]$''''$, and complex cations of Zn, Cu and Ni of the type [M(NH$_3$)$_4$]$''$ or [M(NH$_3$)$_6$]$''$. The cations are adsorbed when the solution is passed through a column of the cationite SBS in the NH$_4$ form and the anions pass into the filtrate. The passage of NaOH solution through the column releases Zn as zincate, and the passage of HCl solution then releases Cu and Ni. *Procedure*— The alloy (0·1 to 0·2 g) is dissolved in 10 to 15 ml of aqua regia, water is added and the liquid is filtered. The acid is neutralised with aq. NH$_3$, and a few drops of HCl solution are added to dissolve the ppt. To the clear solution is added 6 per cent. Na$_4$P$_2$O$_7$ solution until the ppt. initially formed redissolves. Concentrated aq. NH$_3$ is then added in excess and the solution is passed at 6 ml per min. through SBS cationite previously treated with aq. NH$_3$. About 250 ml of water are run through to free the cationite of Fe, Al, Cr, Mn and Mg. To obtain the Zn, 125 to 150 ml of 5 per cent. NaOH solution are passed through at 4 ml per min. until the filtrate gives no reaction for Zn. The Zn can be determined by means of methyl violet and NH$_4$SCN. The solution is evaporated to 100 ml, then neutralised and made up to 200 or 250 ml in a calibrated flask. A 1-ml aliquot is diluted to 5 ml with water and treated successively with 1 ml of 1 N HCl, 0·5 ml of 0·05 per cent. methyl violet solution and 2 ml of 10 per cent. NH$_4$SCN solution, mixing after each addition. The colour is compared with that of standards containing 0 to 0·005 mg of Zn, prepared from pure ZnSO$_4$.7H$_2$O; intervals of 0·0005 mg or less can be used. The colour is green in the absence of Zn and passes through dark blue to violet as the zinc content is increased. The method is applicable to zinc contents of 0·05 to 1·0 per cent. The methyl violet - thiocyanate method is satisfactory in the presence of Al and can be applied without the separation on the cationite by attacking the alloy with NaOH solution and filtering, etc.   G. S. SMITH

1270. Determination of zinc in magnesium alloys by a polarographic method. I. V. Izvekov and N. T. Movchan. *Tr. Krȳmsk. Fil. Akad. Nauk, SSSR*, 1953, **4** (1), 83–89; *Referativnȳĭ Zh., Khim.*, 1955, Abstr. No. 14,207.—The magnesium alloy is dissolved in the minimum amount of HCl and HNO$_3$, and the solution is mixed with a solution containing 200 ml of 25 per cent. aq. NH$_3$, 200 g of NH$_4$Cl, 60 g of citric acid and 50 ml of 1 per cent. agar solution in 1 litre of water. The solution is centrifuged, a crystal of Na$_2$SO$_3$ is added and Zn is determined polarographically from its wave with $E_{\frac{1}{2}}$ of $-1\cdot1$ V. The calibration curve for zinc concn. of 20 to 120 mg per litre in the presence of Mg, Fe and Al is linear. The relative error of determining 0·5 per cent. of Zn in an alloy is ±2 per cent.   G. S. SMITH

1271. Determination of zinc in presence of iron and nickel. J. Lowen and A. L. Carney (Massachusetts Inst. Techn., Lexington, Mass., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1965.—An accurate determination of Zn in ferrites can be effected by passing the soln. of chlorides of Fe$'''$, Zn$''$ and Ni$''$ in conc. HCl through an ion-exchange column of Amberlite IRA-400, or Dowex 1, and eluting with 12 N HCl (25 to 50 ml) to remove Ni, then with 0·5 N HCl (100 ml) to remove Fe, and finally with 0·005 N HCl (150 to 200 ml) to remove Zn. After

any traces of Fe have been complexed with tartrate, Zn is determined by pptn. at 100° C with 3 per cent. quinaldic acid at pH 7 and weighing as Zn(C$_{10}$H$_6$O$_2$N)$_2$.H$_2$O.   W. J. BAKER

1272. Direct volumetric determination of total zinc in mixed paint pigments with ethylenediamine-tetra-acetic acid. M. H. Swann and M. L. Adams (Paint and Chem. Lab., Aberdeen Proving Ground, Md., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 2005.— A rapid procedure for determining total zinc in a mixture of pigments is described that does not involve pptn. with H$_2$S. The sample (1 g) is dissolved in a buffered soln. (pH 10) of NH$_4$Cl and aq. NH$_3$, the insol. pigments being filtered off. The filtrate and an equal vol. of standard ZnO soln. are then titrated, separately, with 0·2 N EDTA (disodium salt) to a blue end-point, with Eriochrome black T indicator. In the presence of much chromium, the end-point is from orange - red to green. The procedure is slightly modified if the sample contains ZnS. The accuracy is equal to that of existing methods.   W. J. BAKER

1273. New micro-reactions for zinc, cadmium and permanganate ions. G. V. Medoks and L. V. Eferova. *Uch. Zap. Saratovsk. Univ.*, 1954, **34**, 121–125; *Referativnȳĭ Zh., Khim.*, 1955, Abstr. No. 14,208.—Tetraphenylphosphonium chloride, (C$_6$H$_5$)$_4$PCl, gives with aq. solutions of ZnCl$_2$ and CdCl$_2$ difficultly sol. cryst. double salts, *e.g.*, [(C$_6$H$_5$)$_4$P][ZnCl$_3$(H$_2$O)], and with aq. soln. of MnO$_4'$ cryst. (C$_6$H$_5$)$_4$PMnO$_4$. The minimum amounts detectable (in μg) and the limiting dilutions are: for Zn, 0·57 and 1 in 8700 (Al$'''$, Cd$''$, I$'$, NO$_3'$, S$_2$O$_8''$ and Cr$_2$O$_7''$ interfere); for Cd, 0·28 and 1 in 1800 (Cr$_2$O$_7''$, I$'$ and S$_2$O$_8''$ interfere); for MnO$_4'$, 0·21 and 1 in 24,000 (Zn$''$, Cd$''$, Al$'''$, NO$_3'$, I$'$, SCN$'$, S$_2$O$_8''$, Cr$_2$O$_7'$ and CrO$_4''$ do not interfere).   G. S. SMITH

1274. Coulogravimetric determination of zinc and cadmium. W. N. MacNevin and R. D. McIver (McPherson Lab., Ohio State Univ., Columbus, Ohio, U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1994–1995.—A soln. containing Zn and Cd can be analysed quant. by electro-deposition of the Zn and Cd together on a mercury cathode in 1 M KCl, beginning the electrolysis at $-1\cdot45$ V *vs.* the S.C.E. The coulometer (100 ml, 0·25 M K$_2$Cr$_2$O$_7$) is read when the current is const. at 0·2 to 0·6 mA. The washed and dried deposit is weighed and the amount of each element is calculated by solving simultaneous equations. The absolute error (caused mainly by large variations in the residual current) is $\simeq\pm0\cdot6$ per cent. for both Zn and Cd. The speed of stirring must be rigidly controlled.   W. J. BAKER

1275. Photochemical estimation of mercuric chloride by Eder's reaction with ceric ion as sensitiser. M. N. Sastri and C. Kalidas (Chem. Lab., Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1955, **148** (1), 3–6.—The reaction between HgCl$_2$ and ammonium oxalate is sensitised by Ce^{IV}. Quantitative pptn. of calomel is rapid when the mixture is exposed to a high-pressure mercury lamp. The reaction is adapted to the volumetric estimation of HgCl$_2$. *Procedure*—To a soln. of HgCl$_2$ are added ammonium oxalate, $\simeq$ four times the theoretical quant. for reduction, and 0·1 ml of freshly prepared

0·01 M ceric ammonium nitrate soln. The mixture is exposed to the mercury lamp for 15 to 20 min., and then excess of I soln. is added. The mixture is shaken for a few min. until no ppt. remains, then the excess of I is titrated with $Na_2S_2O_3$ soln. Good agreement is found with the results obtained by the formaldehyde reduction method.   J. H. WATON

1276. Isotope analysis using dimethylmercury. V. H. Dibeler (Nat. Bur. Stand., Washington, D.C., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1958–1959.—A simple apparatus and procedure for the complete conversion of milligram amounts of Hg into $Hg(CH_3)_2$, and the use of the $Hg(CH_3)_2$ for mass-spectrometric analysis of isotopes are described. The prep. of $Hg(CH_3)_2$ involves the direct combination of Hg and Cl, followed by reaction of the $HgCl_2$ with a slight excess of $Zn(CH_3)_2$. Values for the abundance ratios of a slightly contaminated sample of ^{198}Hg are in good agreement with those obtained from careful measurements on mercury vapour. The advantages of using $Hg(CH_3)_2$ for the mass spectrometry of isotopes are indicated.

W. J. BAKER

1277. Colorimetric method of determining traces of boron. L. M. Kul'berg and T. I. Badeeva. *Ukr. Khim. Zh.*, 1954, **20** (5), 555–563; *Referativnyĭ Zh., Khim.*, 1955, Abstr. No. 14,240.—The method is based on the acceleration by H_3BO_3 of the formation of an azomethine compound by the interaction of H-acid and salicylaldehyde. To determine B in solutions of natural salts, 0·5 ml is mixed with 3·5 ml of a solution containing 50 g of $MgCl_2$, 30 g of NaCl, 20 g of KCl and 400 ml of N acetic acid in 1 litre, and with 0·5 ml of a reagent solution prepared by mixing 1 vol. of a 5 per cent. ethanolic solution of salicylaldehyde with 13 vol. of a 1 per cent. aq. solution of H-acid. The solution is diluted to exactly 5 ml and kept in the dark for 90 min. The extinction is then measured at 420 mμ. The content of B is found from a calibration curve. Boron can be determined in the presence of F' without preliminary separation.   G. S. SMITH

1278. Rapid determination of alumina in vanadium salts. A. Hegedüs. *Kohász. Lapok*, 1954, **9** (7), 333–335; *Referativnyĭ Zh., Khim.*, 1955, Abstr. No. 11,861.—Vanadium mud (1 to 2 g) is dissolved in 20 ml of dil. H_2SO_4 (1 + 1) and 5 ml of conc. HCl, then 0·1 g of boric acid is added. The soln. is evaporated until strong fuming starts, the residue is treated with 50 ml of water, and the SiO_2 is filtered off. The filtrate is boiled for 10 to 15 min. with 10 ml of 30 per cent. NaOH soln., 50 mg of Fe (as $FeCl_3$) and $\simeq 0·3$ g of $NaHSO_3$. The soln. is then cooled, mixed with 50 ml of 30 per cent. NaOH soln. and boiled for 10 to 14 min. The suspension so obtained is diluted to 500 ml and treated as (*i*) or (*ii*) below. (*i*) The suspension (400 ml) is filtered, neutralised to phenolphthalein with H_2SO_4, made slightly alkaline and then boiled with 5 g of NH_4Cl to ppt. $Al(OH)_3$. The ppt. is filtered off, washed with cold water and boiled together with the filter in 50 ml of 0·1 N H_2SO_4. The soln. is mixed with 50 ml of 5 per cent. KF soln. and the excess of acid is titrated with 0·1 N NaOH, with neutral red as indicator. The time taken is 1·5 hr. (*ii*) The suspension (50 to 100 ml) is filtered and 20 to 30 ml, dependent on the supposed alumina content, of 0·05 N EDTA (disodium salt) are added. The soln. is neutralised to phenolphthalein with N H_2SO_4 and a few drops of acid are added in excess. The pH is brought to between

6 and 6·3 by the addition of 5 ml of a buffer soln. containing 274 g of ammonium acetate, 109 g of sodium acetate and 6 ml of glacial acetic acid in 1 litre. An indicator mixture (0·5 g) (1 pt. of Eriochrome cyanine R and 500 pt. of KNO_3) is added and the bright-yellow soln. is titrated at 70° C with 0·05 N $ZnSO_4$ to a lilac - red end-point. A similar amount of 0·05 N EDTA (disodium salt) is titrated at the same time and the difference is calculated to Al (1 ml $\equiv$ 1·345 mg). The time taken is 1 hr.   G. S. SMITH

1279. Absorptiometric determination of alumina in glass sands. P. Poole and D. D. Segrove. *J. Soc. Glass Tech.*, 1955, **39** (189), T205–210.—The method depends on the measurement (Spekker) of the absorption in the yellow - green region due to the colour formed with the reagent aluminon. *Procedure*—The powdered sample (0·1 g) is decomposed with 5 g of HF (40 per cent.) and 5 drops of conc. H_2SO_4 and the residue is fused with 0·5 g of Na_2CO_3. The fusion product is heated with 5 ml of conc. HCl, then extracted with water and made up to 100 ml. To an aliquot portion (50 to 10 ml for a sample containing 0·1 to 2 per cent. of Al_2O_3) are added 1 drop of a 1 per cent. solution of p-nitrophenol and aq. NH_3 to give a yellow colour (pH 4·2 to 4·5), which is just dispelled with a 50 per cent. v/v solution of HCl. To this solution are added 16 drops of 1 per cent. thioglycollic acid (to prevent interference by Fe_2O_3) and 12 ml of aluminon reagent (0·25 g in 250 ml of warm water, with 5 g of acacia, 87 g of ammonium acetate and 126 ml of 50 per cent. v/v HCl, the mixture being made up to 500 ml and filtered). The product is heated at 100° C for 10 min., then cooled and made up to 100 ml. and the absorption is measured in a Spekker spectrometer, with a tungsten-filament lamp and a Kodak filter 555. Interference is given by TiO_2 if the original sample contains $>$0·05 per cent. This method is rapid (2·5 to 3 hr.) and gave results for 7 glass sands which agreed well with those by the slower conventional gravimetric and oxine methods.   J. A. SUGDEN

1280. Fluorescent detection of thallium and mercury. K. P. Stolyarov (A.A. Zhdanov Leningrad State Univ.). *Zh. Anal. Khim.*, 1955, **10** (5), 293–298.—*Detection of thallium*—Various fluorescent methods are discussed and one based on the formation of a compound of NH_4I with Tl is described. A drop of the solution is mixed with a drop of 0·5 N NH_4I on a glass slide and allowed to dry slowly. Examination in the field of an ultra-violet microscope shows a yellow or turquoise-blue photoluminescence. The colour is yellow with 20 mg of Tl per ml, blue at 0·1 mg per ml and violet - blue at 0·0012 mg per ml under light of wavelength 313 mμ. The limiting concn. is 1 in 10,000,000, and the limiting ratios of Tl to Cd, Zn and Ni are 1:1,000,000, 1:10,000 and 1:10,000, respectively. Interference is caused by Cu and Fe··· but not by Fe·· and most other elements. *Detection of mercury*—Methods based on the fluorescence of mercurous chloride, bromide and borate are described.

G. S. SMITH

1281. Co-precipitation of thallium with mercury in the tetrathiocyanatodiamminochromate form. N. T. Voskresenskaya (M. V. Lomonosova Moscow State Univ.). *Zh. Anal. Khim.*, 1955, **10** (4), 222–227.—The solubility at 18° C in water of $Tl[Cr(SCN)_4(NH_3)_2]$, which is pptd. from acid solutions of Tl· salts by Reinecke's salt, is $8·7 \times 10^{-4}$

mole per litre, as found by the use of ^{204}Tl. The concentration of Tl from dil. solutions can be effected by co-pptn. with $Hg^{..}$. Small amounts of Tl can be determined by this means in felspar and other minerals.   G. S. SMITH

1282. Organic co-precipitants. III. Co-precipitation of thallium. V. I. Kuznetsov and G. V. Myasoedova (V. I. Vernadskiĭ Inst. Geochem. and Anal. Chem. Acad. Sci. USSR, Moscow). *Zh. Anal. Khim.*, 1955, **10** (4), 211–216.—Thallium in the form $TlCl_4'$ at concn. $\not< 1$ in 10^{10} in $0.2 N$ HCl is quant. co-pptd. with the ppt. formed by *p*-dimethylaminoazobenzene and methyl orange. Antimony in the form $SbCl_6'$, $AuCl_4'$, Mo and W (particularly as heteropoly acids) and, partially, $Fe^{...}$, are also pptd. Thallous ions are not pptd., hence separation of Tl from all other elements is effected by a co-pptn. of the interfering ions with the organic ppt. in the presence of $Tl^.$, which remain in solution, treatment of the filtrate with chloride of lime to give $TlCl_4'$, and a further co-pptn. to obtain Tl only. The method is applied to the determination of 10^{-6} to 0.1 per cent. of Tl in granite and other silicates.   G. S. SMITH

1283. Use of ion-exchange methods for determining thallium and indium in products from the treatment of non-ferrous metal ores. L. B. Ginzburg and É. P. Shkrobot (State Inst. Non-Ferrous Metals). *Zavod. Lab.*, 1955, **21** (11), 1289–1294.—The cationite SBS adsorbs Tl, but not Sb, from 20 per cent. NaOH solutions and from acid (pH 3 to 5) solutions containing citric, tartaric or oxalic acid, or sodium pyrophosphate. *Determination of Tl in zinc and lead dusts*—The sample (0.5 to 1 g) is heated for 10 to 15 min. with 20 to 25 ml of conc. HCl, 3 to 4 ml of HNO_3 are added, and the liquid is evaporated to dryness. The residue is heated with 20 to 25 ml of 10 per cent. HCl, the solution is cooled and the $PbCl_2$ is filtered off. For the alkaline extraction method, a portion of the solution is treated with 5 g of tartaric acid to form complexes with Fe, Cu, Zn, Cd, Pb and Al, and NaOH solution is added in excess. The solution, diluted to 50 to 60 ml, is passed through a column of SBS at the rate of 4 or 5 ml per min., and the column is washed first with 5 per cent. tartaric acid solution and then with water. For the acid extraction method, the solution is first treated with 5 to 7 g of tartaric or citric acid and then with 2 to 3 g of sodium pyrophosphate. If the pyrophosphate is added first, difficultly sol. zinc pyrophosphate is pptd. The liquid is then passed through the cationite column. To obtain the Tl, the column is washed with 50 to 100 ml of dil. HCl (1 + 1). A portion of the filtrate containing $\not< 1$ µg of Tl is mixed with 0.2 ml of 10 per cent. $NaNO_2$ solution, diluted 5 times with water after 5 min., treated with 10 drops of 0.2 per cent. crystal violet solution, and then extracted with 10 ml of toluene. The colour intensity of the toluene layer is measured with a photocolorimeter and the content of Tl is calculated from a calibration curve. The cationite is partially attacked by NaOH, but the alkaline extraction method is preferred if the sample contains much Cu. *Determination of Sb and Tl in zinc electrolytes*—The electrolyte (10 to 20 ml) is treated with 5 g of citric or tartaric acid and 2 to 3 g of sodium pyrophosphate, the solution is diluted to 50 ml and passed through the cationite column, the column is washed 3 or 4 times with 5 per cent. citric or tartaric acid solution, and then with water, and the filtrate and wash water are collected in a 100-ml calibrated flask. The Tl is

extracted and determined as described above. The Sb in the filtrate is determined by mixing 10 to 20 ml with a similar vol. of conc. HCl, adding several drops of $FeCl_3$ solution and then $SnCl_2$ solution to decolorise. The solution is mixed with 1 ml of 10 per cent. $NaNO_2$ solution and, after 5 min., its own vol. of water. Urea solution (50 per cent.) (0.5 ml) is added and then 10 drops of 0.2 per cent. crystal violet solution, and the coloured antimony complex is extracted with toluene and examined with a photocolorimeter. *Determination of Tl in metallic Cd*—A 0.5 to 1-g sample of Cd is dissolved in 10 to 15 ml of conc. HCl and 1 ml of HNO_3, the liquid is evaporated to dryness, and the residue is dissolved in water. An aliquot portion of this solution is treated with 5 to 6 g of citric or tartaric acid and neutralised to methyl orange with NaOH solution. The solution is passed through the cationite column and Tl is determined as described above. *Determination of In in lead and zinc dusts by a fluorescent method*—The cationite SBS is used to separate In from the elements that interfere in the 8-hydroxyquinoline fluorescence method. The metal dust (0.5 g) is dissolved in aqua regia, the solution is evaporated with H_2SO_4, the residue is boiled with 20 to 30 ml of water, the solution is cooled, and $PbSO_4$ is filtered off and washed with dil. H_2SO_4. A portion of the filtrate is treated with 5 to 7 g of sulphosalicylic acid and then with aq. NH_3 solution until the colour becomes orange yellow. The solution is diluted to 50 ml and passed through a column of the adsorbent at the rate of 4 or 5 ml per min. The column is washed first with 5 per cent. sulphosalicylic acid solution, which has been adjusted to a pH of 9 to 10 with aq. NH_3 solution, and then with water. Indium is removed from the column by means of 50 to 100 ml of $2 N$ HCl, an aliquot portion of the filtrate is evaporated to dryness, the dry residue is dissolved in 1 ml of $0.2 N$ HCl, and 1 ml of 20 per cent. hydroxylamine solution, 1 ml of 2 per cent. thiourea solution and 10 ml of $0.2 M$ K H phthalate are added. The solution is diluted to 20 ml with water in an Eggertz cylinder and set aside for 15 to 20 min., then 3 ml of 0.2 per cent. 8-hydroxyquinoline in chloroform solution are added and vigorously shaken. The fluorescence intensity is matched with that of a standard solution of indium.   G. S. SMITH

1284. An improved method for operating ion-exchange resin columns in separating the rare-earth elements. W. E. Nervik (Univ. California, Radiation Lab., Livermore Site, U.S.A.). *J. Phys. Chem.*, 1955, **59** (8), 690–695.—Commercial 12 per cent. cross-linked Dowex-50 cation-exchange resin of − 400 mesh is graded to obtain that portion which settles between 1.0 and 1.5 cm per min. in water. The resin is washed with $6 M$ NH_4SCN, water, $6 N$ HCl and water again. Finally it is treated with ammonium lactate and stored in water. The column is set up and its temp. brought to 90° C with a heating jacket. The resin is boiled with water and, while hot, is put in the column. An eluting agent (100 ml) consisting of $1 M$ ammonium lactate buffer at the required pH is poured through the column. A mixture of purified rare-earth activities is adsorbed on a portion of hot resin and this is added to the column. Gradient elution is carried out by passing on to the column a soln. of buffer at pH 3.19 to which is added continuously, with stirring, a soln. of a buffer at pH 7. Samples of the eluate are collected at 3-min. intervals with a fraction cutter. A drop of each fraction is evaporated on an aluminium plate and the activity

of each sample is counted. A good separation of the rare earths is obtained.   C. A. SLATER

1285. Molar extinction coefficients of the rare earths and their use in analysis. L. Holleck and L. Hartinger (Chem. Inst., Hochsch., Bamberg, Germany). *Angew. Chem.*, 1955, **67** (21), 648–651. —Spectrophotometric determinations were made of the absorption spectra of the chlorides of Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb, and determinations of their extinction values were made at a number of separate wavebands for each element. A detailed discussion is given of the quant. analysis of solutions of chlorides of the rare-earth elements by methods in which the test solution is diluted until its absorption agrees with that of a standard solution of the element, or until it no longer gives absorption. A table is given to show the ranges of concn. over which the solution of each element obeys the Beer - Lambert law, the ranges being given for several bands with each element. The effect of the simultaneous presence of a number of the rare-earth elements is discussed, and examples are given where a prior separation of the elements (by ion exchange) is necessary (*e.g.*, cerite earths from yttria earths and individual separation of the yttria earths). Interferences with each element by other rare-earth elements at particular wavelengths are tabulated. With suitable choice of wavelength, simultaneous determination can be made of a number of the rare earths in a common solution (*e.g.*, all the cerite earths). The absorption bands of Tb are too weak for practical analysis. Gadolinium normally gives excessively high results and a method for their correct evaluation is described. In general, apart from variations caused by certain individual mixtures and by the factors of relative concn., estimations are accurate to within 1 per cent. in the presence of 2 to 3 elements and to within 2 per cent. with >3 elements.
          H. L. WHITEHEAD

1286. Mercuro-reductimetric determination of cerium. V. M. Tarayan and M. G. Ekimyan. *Nauch. Tr. Erevansk. Univ.*, 1954, **44**, 87–94; *Referativnȳi Zh., Khim.*, 1955, Abstr. No. 14,216.— Ceric sulphate is titrated with mercurous perchlorate solution, with 1 drop of $0.02 N$ $AuCl_3$ as catalyst and N-phenylanthranilic acid as indicator in 0.5 to $6 N$ H_2SO_4. The reaction is stoicheiometric:— $2Ce^{IV} + Hg_2^{I} \rightarrow 2Ce^{III} + 2Hg^{II}$.   G. S. SMITH

1287. Determination of free acid in solutions of quadrivalent cerium salts. V. V. Oshchapovskii (Lvov Polytech. Inst., Ukrain. SSR). *Ukr. Khim. Zh.*, 1955, **21** (3), 384–387.—Free acid in 0.05 to $0.1 N$ $Ce(SO_4)_2$ or $Ce(NO_3)_4$ is determined by titrating the eluate from a Wofatit II column, and subtracting the amount of acid corresponding to the known content of Ce^{IV}; this method cannot be applied to solutions of acidity $> 0.2 N$. Addition to the Ce^{IV} solutions of a 4-fold excess of neutral aq. NaF, followed after 5 min. by titration with $0.1 N$ NaOH (phenolphthalein) gives good results for free acidity measurements, but requires the use of wax-coated vessels. The most convenient method consists in adding a 2-fold excess of K oxalate and heating at $70°$ C for 20 to 25 min., when Ce^{III}, produced by the reduction of Ce^{IV} by C_2O_4'', is pptd. as $Ce_2(C_2O_4)_3$; free acid is then titrated.   R. TRUSCOE

1288. Radiochemical separation of actinium and its daughters by means of lead sulphate. N. E. Rogers and R. M. Watrous (Monsanto Chem. Co.,

Miamisburg. Ohio, U.S.A.). *Anal. Chem.*, 1955, **27** (12), 2009–2012.—The radiochemical separation of ^{227}Ac, ^{227}Th, ^{223}Ra, Rn, etc., from rat urine can be effected by co-pptn. of these elements on $PbSO_4$ in a dil. HNO_3 soln., at $75°$ C, of the dried urine salts. The radioactive $PbSO_4$ is removed by centrifugation, dissolved in conc. HCl, the soln. is evaporated to dryness and the residue is dissolved in dil. HCl, the soln. being transferred to the beaker in which the pptn. was made. The lead is removed by two pptn. with H_2S at pH 3 to 3.5, the two filtrates being combined and evaporated to dryness. The residue is dissolved in conc. HNO_3, two successive evaporations to small vol. are made and, finally, the activity of an aliquot (dried at $700°$ C on a slide) of the diluted soln. is determined by an α-count within the range of 10^3 to 5×10^4 counts per min. The ignited aliquot is set aside for 3 to 4 hr. to attain equilibrium before a count is made. Recovery of ^{227}Ac-in-equilibrium in the final filtrate is $\simeq 90$ per cent.; the activity loss is $\simeq 2$ per cent., mostly ^{227}Th. The actinium fraction includes only a small amount of urine salts co-pptd. with the $PbSO_4$. The method requires about 8 hr.
          W. J. BAKER

1289. Inherent errors and lower limits of activity detection in gas-phase proportional counting of carbon-14. D. R. Christman and A. P. Wolf (Brookhaven Nat. Lab., Upton, Long Island, N.Y., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1939–1941.— The precision of the method of ^{14}C analysis by measurement with gas proportional counters is discussed from the standpoint of the type and magnitude of the errors inherent in the method. The errors discussed fall into two classes—(*i*) those that are systematic and affect all analyses equally, hence are of importance only with respect to the absolute activity values, and (*ii*) those that differ for each experiment; these contribute directly to the deviation in results between samples. An approximate value is assigned to each type of error discussed. The lower limit of activity detection was found to be 2 counts per min. under the conditions prescribed.   D. G. HIGGS

1290. Method for the colorimetric estimation of free cyanide. Preliminary communication. G. Heilmann (Metallograph. Lab., Degussa, Pforzheim, Germany). *Z. anal. Chem.*, 1955, **148** (1), 29–31.— Free CN' can be estimated colorimetrically by the deepening of colour produced with a soln. of $K_2[Ni(CN)_4]$. The method is suitable for the analytical control of CN' in electroplating baths, and for the evaluation of the formulae of complex cyanides. Considerable deviation from predicted results is found in alkaline soln. when the complexed metal can form hydroxy complexes.
          J. H. WATON

1291. The detection of dicyanogen on the micro scale. A contribution to the chemistry of specific, selective and sensitive reactions. F. Feigl and L. Hainberger (Minist. Agric., Rio de Janeiro, Brazil). *Analyst*, 1955, **80**, 807–811.—The red colour reaction of Komarowsky *et al.* (*Z. anal. Chem.*, 1934, **96**, 23) between 8-hydroxyquinoline (I) and dicyanogen generated in the soln. occurs also when gaseous $(CN)_2$ reacts with a conc. soln. of KCN containing I. This is the basis of a specific test for $(CN)_2$, $1 \mu g$ being detectable. The open end of a micro test-tube is closed with a disc of filter-paper impregnated with I (prepared by immersing the paper in a 1 per cent. soln. in ether and drying) and moistened with a drop of 25 per cent. KCN soln.

The test substance in the tube is then heated over a micro burner. To increase the yield of $(CN)_2$ from heat-stable cyanides, *e.g.*, NaCN and KCN, or from those decomposing only at high temp., *e.g.*, $Zn(CN)_2$ and $Cd(CN)_2$, the sample is first evaporated with ethanolic $HgCl_2$ soln. to convert the cyanides into $Hg(CN)_2$, which readily yields $(CN)_2$. Some characteristic differences in the behaviour of analogously constructed organic compounds of N in splitting off $(CN)_2$ and the participation of pyrolytically derived $(CN)_2$ or HCN in the Beilstein and Lassaigne tests are discussed.   A. O. JONES

1292. Estimation of silica. A. K. Majumdar and S. Banerjee (College Engng and Tech., Bengal, Calcutta, India). *Anal. Chim. Acta*, 1955, **13** (5), 424–426.—In the procedure described, a sample containing from 3 to 10 mg of SiO_2 is fused with Na_2CO_3 (100 mg), the cool melt is treated with warm water, and the SiO_2 in the resulting soln. is converted into molybdosilicic acid by the addition of ammonium molybdate and conc. HCl. A vol. of either 2 per cent. 5:6-benzoquinaldine or 1 per cent. 8-hydroxyquinaldine (as hydrochlorides) is then added to the warm soln., under controlled conditions of acidity. The pptd. stable organic salt ($H_4SiO_4.12MoO_3.4C_{14}H_{11}N$ or $H_4SiO_4.12MoO_3$. $4C_{10}H_9ON$) is then filtered off and weighed after drying at 110° to 150° C, or after conversion into $SiO_2.12MoO_3$ by ignition at 550° C with free access of air.   W. J. BAKER

1293. Determination of silica in fluorosilicates without removal of fluorine. H. R. Shell (Bur. of Mines, U.S. Dept. Interior, Norris, Tenn., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 2006–2007.—In the analysis of fluorosilicates (including minerals, phosphate rock, etc.), the SiO_2 can be determined quant., without removal of F', by the usual gravimetric procedure if $\simeq 500$ mg of Al''' ($\equiv 4.5$ g of $AlCl_3.6H_2O$) are added to the dil. HCl soln. before the evaporations. A correction is made for the SiO_2 content of the added salt. Recovery of SiO_2 is as complete as with the zinc oxide fusion method, the value for SiO_2 (as always) being $\simeq 0.2$ per cent. low.   W. J. BAKER

1294. Trihydroxyfluorone derivatives as reagents for tin and antimony. V. A. Nazarenko and N. V. Lebedeva. *Zh. Anal. Khim.*, 1955, **10** (5), 289–292. —2:3:7-Trihydroxy-6-fluorone derivatives with a substituent in position 9 are sensitive colorimetric reagents for Sn^{IV} and Sb^{III}. Sixteen such derivatives are synthesised from triacetoxyanthraquinone and the corresponding aldehyde. *Determination of tin with* 2:3:7-*trihydroxy*-9-p-*nitrophenyl*-6-*fluorone*—To 10 ml of the solution to be tested are added 0.5 g of NaCl and sufficient H_2SO_4 or HCl to make the solution 0.1 N. The solution is mixed with 0.5 ml of 1 per cent. gelatin solution, and then with 0.5 ml (for 0.5 to 10 μg of Sn) or 1 ml (for 10 to 30 μg of Sn) of 0.05 per cent. solution of the reagent in 96 per cent. ethanol containing 1 ml of 6 N HCl in 100 ml. The extinction is measured after 45 min., with a green filter (530 mμ), in a 10 to 20-mm cell, and compared with that of a similar solution but without Sn. The tin concn. is found from a calibration curve. Extinction and concn. are linear over the range 0.5 to 30 μg of Sn. To separate Sn from other elements, the Sn is distilled with excess of Br from a H_2SO_4 - H_3PO_4 solution and free Br is removed from the distillate by means of phenol; Sb does not interfere under these conditions. *Determination of antimony with*

2:3:7-*trihydroxy*-9-*phenyl*-6-*fluorone*—The solution (10 ml), N in H_2SO_4, is mixed with 1 ml of gelatin solution and 0.5 ml of the reagent in 96 per cent. ethanol containing 1 ml of 6 N HCl in 100 ml, and the extinction is measured after 30 min., with a green filter. Extinction and concn. are linear over the range 0.5 to 20 μg of Sb. To separate Sb from interfering elements, the Sb is extracted as the pyridine - iodide complex from 8 N H_2SO_4 containing 5 per cent. of tartaric acid by means of ether. The ether extract is then shaken with N H_2SO_4 to obtain Sb in the aq. phase.   G. S. SMITH

1295. Simple coulometer method for tin coating determination. J. Monvoisin and M. Le Blanc (J. J. Carnaud & Forges de Basse-Indre, Boulogne-Billancourt, France). *Tin Uses*, 1955, (33), 3–5.— A modification of the coulometer method (*cf. Anal. Abstr.*, 1954, **1**, 2381) dispenses with the use of a high-speed recording potentiometer and enables tin and tin-alloy coating weights to be read directly and separately on a meter which is directly graduated and calibrated in grams of Sn per sq. metre.   S.C.I. ABSTR.

1296. Polarographic determination of lead, tin and cadmium when present together in metallic zinc and zinc electrolytes. F. K. Baev and P. N. Kovalenko (V. M. Molotov Rostov State Univ.). *Zavod. Lab.*, 1955, **21** (10), 1170–1172.—This method, which requires no preliminary separations, is based on the use of two supporting electrolytes. A polarographic wave corresponding to the sum of Pb and Sn is measured in HCl, and the waves due to Pb and Cd are measured in HCl - citric acid. Calculations from these measurements give the separate contents of Pb, Sn and Cd.   G. S. SMITH

1297. The determination of lead in organic material. J. C. Gage (I.C.I. Ltd., Industr. Hyg. Res. Lab., Welwyn, Herts., England). *Analyst*, 1955, **80**, 789–796.—Organic matter is destroyed, first in a current of air at low temp. and then, after addition of $Mg(NO_3)_2$, at 500° C in a current of HNO_3 vapour. A simple and convenient electrically heated apparatus is described. The ash is dissolved in HCl, the soln. is treated with a bicarbonate - citrate soln. and Na diethyldithiocarbamate. The Pb diethyldithiocarbamate is extracted with a mixture of amyl alcohol and toluene. From the extract the Pb is extracted with HCl, this extract is treated with ammoniacal dithizone soln. and the Pb dithizonate is extracted with CCl_4. The CCl_4 soln. is adjusted to a definite vol. and its extinction is measured at 515 mμ. The concn. of Pb is ascertained from a calibration graph prepared with soln. of $Pb(NO_3)_2$ in HCl treated in the same way. The method as described is specific for Pb and precision and recovery are good.   A. O. JONES

1298. Colorimetric determination of lead in atmospheric air. V. A. Morozov. *Gigiena i Sanit.*, 1954, (9), 46; *Referativnÿi Zh., Khim.*, 1955, Abstr. No. 14,220.—With lead salts of lead concn. 0.0025 to 0.025 μg per ml, quinalizarin gives a yellow coloration which changes to pinkish blue as the concn. is increased to 2 μg per ml; Cu, Zn and Fe give similar colorations and must be removed. To test for Pb in dust from the air, a sample collected on filter-paper is boiled for 10 to 15 min. with 3 per cent. aq. HNO_3, the solution is evaporated to dryness, the residue is dissolved in water, and the solution is boiled with 0.2 ml of 25 per cent. aq.

NH$_3$, 0·2 ml of 25 per cent. NH$_4$Cl soln., 0·1 ml of N Na$_2$CO$_3$ and 0·1 ml of N CaCl$_2$. The ppt. is centrifuged, washed with aq. NH$_3$ and water, treated with 10 per cent. aq. NaOH soln. and again centrifuged. The plumbite solution is made just acid with 3 per cent. aq. HNO$_3$, the solution is evaporated to dryness, and the residue is dissolved in water of pH 6·2 to 6·4. Standard solutions are prepared simultaneously. Five drops of 0·002 per cent. quinalizarin in acetone are added to the sample and the standards and the colours are compared after 2 to 3 min.   G. S. SMITH

1299. **Determination of heavy metals by means of hydroxamic acids. Determination of lead with oxalhydroxamic acid.** I. P. Ryazanov and T. I. Badeeva. *Uch. Zap. Saratovsk. Univ.*, 1954, **34**, 208–210; *Referativnyĭ Zh., Khim.*, 1955, Abstr. No. 14,219.—The lead salt of oxalhydroxamic acid (CONHOH)$_2$ is almost insol. in water, easily sol. in mineral acids, somewhat sol. in acetic acid, almost insol. in sodium acetate solution, and insol. in caustic alkalis, alcohol, acetone and benzene. To determine Pb in lead nitrate solution, for each 10 ml containing $\simeq$20 mg of Pb are added, in the cold, 10 to 15 ml of a 1 per cent. solution of the sodium salt of the acid, the ppt. is filtered off after 18 hr. in a sintered-glass crucible, washed with cold water until the washings give no reaction for the hydroxamate, and then dried to const. wt. at 155° to 160° C. The factor for (CONHO)$_2$Pb to Pb is 0·6371. With 0·0219 g of Pb the results of four determinations were correct to $\pm$0·0001 g.
                        G. S. SMITH

1300. **Determination of lead in lead sulphide ores and concentrates.** C. A. Goetz and F. J. Debbrecht (Iowa State College, Ames, Iowa, U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1972–1975.—The sample ($\equiv$ 0·1 to 0·15 g of Pb) is dissolved in boiling 72 per cent. HClO$_4$ (15 ml) and the Pb in the cooled dil. soln. ($\simeq$150 ml) is separated from all other elements by electro-deposition (3 amp. for 1 hr.) as PbO$_2$ in the presence of conc. HNO$_3$. After dissolution of the washed PbO$_2$ in 25 ml of water containing conc. HNO$_3$ (0·25 ml) and hydroxylamine hydrochloride (0·5 g), the Pb is titrated directly with 0·02 M disodium dihydrogen 1:2-diamino*cyclo*hexane-NNN′N′-tetra-acetate (HexaVer) in the presence of tartrate at pH 10. The end-point is from violet to blue-green (Eriochrome black T indicator). An analysis takes $\simeq$1 hr., the error being 0·001 per cent. Interference by As, Sb and Sn is obviated by removing these metals as volatile bromides before electro-deposition of Pb.   W. J. BAKER

1301. **Amperometric analysis with the use of cupferron. I. Determination of titanium.** Yu. I. Usatenko and G. E. Bekleshova (Dnepropetrovsk Chem.-Tech. Inst.). *Zavod. Lab.*, 1955, **21** (7), 779–782.—Cupferron in various concn. in KCl or NaCl, or in 0·1 to 3 N H$_2$SO$_4$, gives a well-defined polarographic wave with a half-wave potential of about 0·6 to 0·7 V (*vs.* the S.C.E.) on a rotating platinum micro-anode. The wave height is proportional to the cupferron concn. Titanium can be titrated amperometrically at 0·8 V with a standard cupferron solution prepared by dissolving 3 g of cupferron in a cooled aq. solution of 0·5 g of phenacetin (dissolved by heating), and then making up to 1 litre. The solution to be titrated contains 130 ml of the titanium solution, 0·2 N in H$_2$SO$_4$, and 5 g of NaCl. After each determination the platinum micro-electrode is washed with aq. NH$_3$ soln.

and heated in a spirit flame for a few sec. One atom of Ti reacts with 2 mol. of cupferron. To determine Ti in clays, etc., 0·1 g is heated at 1000° C with 0·4 g of Na$_2$CO$_3$ for a few min. The melt is treated with water and HCl, the solution is neutralised with aq. NH$_3$ soln., the ppt. is dissolved by the addition or 1 or 2 drops of 5 N H$_2$SO$_4$ and sufficient excess (about 1 ml) is added to make the solution 0·2 N. After the addition of 5 ml of 1 per cent. EDTA (disodium salt) solution, to form a complex with the Fe, and 5 g of NaCl the solution is titrated with cupferron solution, with a 1-min. interval after the addition of each portion. The results are not affected by the presence of Mn, Al, SiO$_2$ and a sixfold amount of Fe.   G. S. SMITH

1302. **Colorimetric determination of minute amounts of quadrivalent titanium in the presence of large quantities of tervalent iron.** P. Szarvas and B. Csiszár (L. Kossuth Univ., Debrecen, Hungary). *Acta Chim. Acad. Sci. Hung*, 1955, **7** (3–4), 403–410. —A method is described for the determination by spectrophotometry of Ti^{IV} (several μg per ml) in the presence of Fe^{III} (several mg per ml). Identical appropriate volumes (*e.g.*, 1 ml) of the solution to be tested, containing 3 to 100 μg per ml of Ti^{IV} and 0 to 10 mg per ml of Fe^{III} in about 2 N H$_2$SO$_4$, are measured into two 25-ml calibrated flasks. Tiron soln. (1 per cent.) (5 ml) is added, with shaking, to one flask, followed by 0·05 M EDTA (disodium salt) soln. (5 ml) and M Na acetate (10 ml), and the soln. is made up to the mark with water. A similar soln. is made up in the other flask, but the Tiron is omitted. The two solutions thus prepared are compared in 1-cm cuvettes in a Zeiss-Pulfrich photometer, with S42 filters. A working curve is plotted in the usual way with a standard soln. of Ti^{IV}. Beer's law is obeyed by soln. containing up to 160 μg of Ti per ml.   C. A. SLATER

1303. **Determination of oxygen in titanium.** J. Orsag. *Rev. Métall.*, 1955, **52**, 237–239.—The oxygen content was determined by the action of Cl on the metal. Considerable surface oxidation was observed if the samples were obtained by sawing. This error in the oxygen determination can be avoided by a prechlorination after sawing, but before the final attack by Cl for the decomposition. The contaminated sample (4 to 5 g) is heated to dull redness in a current of Cl. After this pretreatment the sample is used for the analysis.
                        CHEM. ABSTR.

1304. **Separation of quadrivalent titanium, zirconium and thorium by paper chromatography. Qualitative and quantitative evaluation of chromatograms.** G. Almássy and Z. Nagy (Inst. Med. Chem., Med. Univ., Debrecen, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1955, **7** (3–4), 325–331.—Solvent systems have been worked out for the separation of Ti^{IV}, Zr^{IV} and Th^{IV}, and R_F values in a number of solvents containing HCl, ethanol and water in different proportions are given. In concentrations as low as 0·01 μg per 0·1 ml, Ti^{IV} may be detected by the use of a solvent containing ethanol and conc. HCl (80:20). For Zr^{IV}, ethanol-conc. HCl-H$_2$O (75:20:5) is used, and for Th^{IV} (79:20:1). Detection is by spraying with ethanolic morin, when the elements show up as coloured spots, or by fluorescence under u.v. light. The method can be made roughly quant. for Ti and Zr by adding FeCl$_3$ soln. (1 per cent., 0·01 ml) to the spots of sample and standards before development.
                        C. A. SLATER

1305. **Use of morin in micro-analysis. II. Detection of quadrivalent zirconium with morin.** G. Almássy (Inst. Med. Chem., Med. Univ., Debrecen, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1955, **7** (3–4), 245–246.—The detection of Zr^{IV} is based on the formation in acid solution of a complex with morin, which gives a yellow fluorescence in u.v. light. Interference by coloured metal ions is eliminated by reduction with zinc powder. To the test-solution (1 ml) is added HCl (1:1; 0·5 ml) and $CuSO_4$ solution (1 per cent.; 1 drop) followed by a little zinc dust. The solution is set aside for 30 sec. or (in the presence of $Fe^{···}$, $Ti^{····}$, VO_3', MnO_4' and CrO_4'') for 1 to 2 min. Ethanolic morin (0·5 per cent.; 2 drops) is added when, in the presence of Zr^{IV}, the soln. turns yellow. One p.p.m. of Zr^{IV} can be detected.

III. Reduction of morin as an informative test in qualitative analysis. G. Almássy. *Ibid.*, 1955, **7** (3–4), 249–251.—It is shown that certain metal ions inhibit the reduction of morin by zinc dust and HCl. This effect is used as an informative test in the qualitative analysis of cations. The slightly acid solution to be tested (1 ml) is treated with HCl (1:1; 0·5 ml), oxalic acid soln. (5 per cent.; 0·5 ml) and zinc dust (of high purity). When the evolution of hydrogen begins, morin soln. (0·5 per cent. in ethanol; 2 to 3 drops) is added. In the presence of cations that prevent reduction the solution remains uncoloured, but with those that do not prevent reduction the soln. turns red. Cations that prevent reduction are $Ag^·$, $Pb^{··}$, $Hg^·$, $Hg^{··}$, $Cu^{··}$, $Bi^{···}$, $Cd^{··}$, $As^{···}$, $Sb^{···}$, $Sn^{··}$, $Ni^{··}$ and $Co^{···}$.

C. A. SLATER

1306. **Use of organic reagents in inorganic analysis. III. Determination of zirconium with some anilic acids and its separation from thorium by solvent extraction.** S. K. Datta (Darjeeling Gov. Coll., India). *Z. anal. Chem.*, 1955, **148** (5), 334–339.—The precipitation of Zr by phthalanilic acids prepared from simple aromatic amines is examined. Quantitative pptn. is achieved by the addition of an alcoholic soln. of anilic acids derived from *o*-nitroaniline (**I**), *p*-nitroaniline (**II**), 1-naphthylamine (**III**) or *p*-toluidine (**IV**) to the zirconium soln. buffered with ammonium acetate or NH_4Cl to a pH of 2·7 to 4·2 for **I** and **II**, 4·6 for **III**, and 3·0 to 4·2 for **IV**. Quantitative separation of Zr from approx. equiv. amounts of Cu, Cd, Al, Cr, Ba, Ca, Zn, Mg and Ti and from a threefold excess of cerite earths is possible by single pptn., and from approx. equiv. amounts of Ni, Co, Fe and U by double pptn. with **I**, **II**, **IV** and the anilic acid derived from *o*-toluidine. Quantitative separation of Zr from Th is achieved by dissolution of the pptd. complex of Th in cold amyl acetate; the complex of Zr remains undissolved.

J. P. STERN

1307. **Diphenic acid as an analytical reagent. I. Determination of thorium by direct weighing method.** G. Banerjee (Darjeeling Gov. Coll., Darjeeling, India). *Z. anal. Chem.*, 1955, **147** (6), 404–409.—Thorium is estimated directly by pptn. with a 0·1 M aq. soln. of diphenic acid in the pH range 4·5 to 8·6. The ppt. has the formula $Th(C_{14}H_8O_4)_2$, and contains 32·59 per cent. of Th or 37·09 per cent. of ThO_2. No interference occurs when Ca, Sr, Ba, Ti, Cr, Al, Ce^{III}, Cu, Ni, Co, Pb, Sn and Mg are present, but Zr must be absent. The addition of small amounts of ammonium acetate allows Th diphenate to be pptd. in the cold. *Procedure*—A soln. containing 0·007 to 0·110 g of ThO_2 is made neutral to Congo red,

diluted to 45 ml and brought to the boiling point. A slight excess of a hot 0·1 M aq. soln. of diphenic acid is added, followed by 10 ml of a 1 per cent. soln. of ammonium acetate. The ppt. appears at once and settles out after the soln. has been slightly warmed. After 5 min. the ppt. is collected on a fine-porosity sintered-glass crucible and washed with hot water, a 0·01 M soln. of diphenic acid and finally with hot ethanol. The ppt. is dried to constant wt. at 110° to 115° C.

II. Separation of thorium from zirconium, titanium and iron and their co-determinations. G. Banerjee. *Ibid.*, 1955, **147** (6), 409–415.—Diphenic acid separates Th and Zr, since Th diphenate is pptd. in the pH range 4·5 to 8·6 and the Zr derivative at pH $<2·0$. Unlike Th diphenate, the Zr ppt. is not stoicheiometric and must be ignited to ZrO_2. In soln. neutral to Congo red, Th may be separated from Ti, and also from Fe^{II} if a double pptn. is used. To separate Th from Fe^{III}, the Fe^{III} must be masked by the addition of ascorbic acid, but can then be pptd. from neutral soln. by adding ammonium diphenate. The following procedure is given for the co-determination of Th, Zr, Fe^{III} and Ti. The soln. of the metals is made neutral to Congo red with aq. NH_3 and then brought to pH 1·8 with 3·5 M HNO_3 or acetic acid and 0·1 g of ammonium acetate, when the Zr is pptd. with 0·1 M diphenic acid soln. The ppt. is washed successively with 0·01 M soln. of the reagent, hot water and ethanol, and ignited to ZrO_2. Ascorbic acid is added to the filtrate and washings and the Th is pptd. from the boiling soln. by the addition of excess of 0·1 M diphenic acid soln.; the estimation of Th is completed as previously described. The filtrate and washings are evaporated to a small vol. and Fe^{III} is pptd. by the addition of a 1 per cent. soln. of ammonium diphenate. The ppt., after being washed, is ignited to Fe_2O_3. From the final filtrate Ti is estimated by the usual pptn. with aq. NH_3.

J. H. WATON

1308. **Direct compleximetric titration of thorium with Versene using SPADNS.** G. Banerjee (Darjeeling Gov. Coll., India). *Z. anal. Chem.*, 1955, **148** (5), 349–354.—Thorium (5 to 35 mg) can be determined by direct titration with 0·025 M aq. Versene [EDTA (disodium salt)] (**I**) in 50 ml of soln. at pH 2·2 to 3·5, with SPADNS (*cf. Anal. Abstr.*, 1956, **3**, 74) as indicator. Interference by Fe is eliminated by the addition of ascorbic acid, of which 1 g prevents interference by 165 mg of Fe^{II} and 75 mg of Fe^{III}. Lithium, Na, K, $NH_4^·$, $Hg^{··}$, Ca, Sr, Ba, Mg, $Co^{··}$, Al, $La^{···}$, $Ce^{···}$, $Cr^{···}$, acetate and VO_3', in concn. $\simeq 10$ times that of Th, do not interfere, but Ag, $Pb^{··}$, $Sn^{··}$, $Ni^{··}$, $UO_2^{··}$, $V^{··}$, $Mo^{···}$, $Sb^{···}$, Bi, $Ce^{····}$, $Ti^{····}$, $Sn^{····}$, F', MoO_4'', citrate, oxalate and tartrate in similar concn. interfere.

J. P. STERN

1309. **The electrolytic separation from thorium nitrate of thorium-C (^{212}Bi) and thorium-B (^{212}Pb) in chloride solution.** A. D. R. Harrison, A. J. Lindsey and R. Phillips (Sir John Cass Coll., London). *Anal. Chim. Acta*, 1955, **13** (5), 459–464.—An electro-deposition procedure for separating Th-C and Th-B from radiochemically "old" samples of $Th(NO_3)_4$ in hot 0·5 N HCl soln. is described. The Th-C is first deposited on either a demountable platinum or nickel cathode (embedded in a polythene disc) at a controlled cathode potential of $\simeq 250$ mV (*vs.* the S.C.E.) and with 0·4 to 1·76 mg of bismuth as carrier. Almost all the Th-C is removed in $\simeq 25$ min., after which the Th-B is

deposited on a fresh cathode by using a current of $\simeq 250$ mA but no controlled cathode potential. The purity of each isotope can be checked from a semi-log curve of activity (corrected) against time. Amounts of the order of 10^{-15} g of Th-C can thus be determined.   W. J. BAKER

1310. Quantitative determination of thorium and uranium in solutions by fluorescent X-ray spectrometry. G. Pish and A. A. Huffman (Monsanto Chem. Co., Miamisburg, Ohio, U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1875–1878.—A rapid and accurate method has been developed in which aq. and org. soln. can be analysed directly. Sample preparation requires only the addition of an internal standard—Sr for aq. soln. and bromobenzene for org. soln. Calibration curves are obtained by plotting the ratios of counts of the element sought to that of the internal standard against the concn. of the element; straight lines were obtained for both Th and U over the range 0 to 250 mg of Th and 0 to 5·0 mg of U per ml of soln. The analytical sample was prepared by adding 1 ml of the appropriate internal standard to the test sample (10 ml) and was placed in the fluorescent X-ray unit. Each sample was set manually at the positions indicated for the sample type and a set of three counts was taken over a predetermined period of time with the apparatus operated at 50 kV and 45 mA. Less than 0·5 hr. was required for each sample and the accuracy was equal to that of the chemical methods.

D. G. HIGGS

1311. Volumetric determination of ammonia by decinormal potassium bromate solution. D. Köszegi and É. Salgó (Inst. Pharm. Chem., Med. Univ., Szeged, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1955, **7** (3–4), 333–342.—Conditions under which the reaction:—

$$2NH_3 + 3KOBr = 3KBr + 3H_2O + N_2,$$
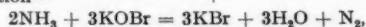
is quant. have been established, and a method for the determination of ammonia and ammonium salts has been worked out; the method is accurate to $\pm 0·09$ per cent. Excess of 0·1 N KBrO$_3$ (40 ml) and KBr (1·5 g) is acidified with 10 ml of 2 N HCl in a closed flask and then made alkaline with 16 ml of 2 N NaOH, thus forming KOBr; the ammonium compound which is to be determined is then added. After 20 min. the solution is acidified and KI is added. The liberated iodine is estimated in the usual way.   C. A. SLATER

1312. Polarographic nitrate determination. R. E. Hamm and C. D. Withrow (Univ. Utah, Salt Lake City, Utah, U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1913–1915.—A new polarographic wave has been found for the induced reduction of NO$_3'$ when present in a soln. of Cr$^{\cdots}$ - glycine complex. The effective concn. range is 1×10^{-5} to $2·5 \times 10^{-3}$ M and the precision is good in comparison with the older methods. The waves for NO$_2'$ and NO$_3'$ are similar.   D. G. HIGGS

1313. Photometric estimation of nitrite with Rivanol [2:5-diamino-7-ethoxyacridine]. M. Svach and J. Zýka (Inst. Anal. Chem., Karlovy Univ., Prague, Czechoslovakia). *Z. anal. Chem.*, 1955, **148** (1), 1–2.—Nitrites can be determined photometrically as the red complex given with Rivanol in the presence of dil. HCl. The nitrite soln., containing $\not> 60$ μg of NaNO$_2$, is introduced into a 50-ml flask, and 10 ml of a 0·5 per cent. soln. of Rivanol are added. After the addition of 15 ml of 6 N HCl, the soln. is made up to the mark and its extinction is measured at 525 mμ, a green filter being used. The nitrite - Rivanol complex is stable for $\simeq 50$ min. The method has been applied successfully to the determination of amyl and ethyl nitrites and to trinitroglycerol.   J. H. WATON

1314. Chromotropic acid as an analytical reagent. III. Interaction of nitrites with chromotropic acid. S. Ya. Shnaĭderman. *Izv. Kievsk. Politekhn. Inst.*, 1954, **14**, 152–155; *Referativnyĭ Zh., Khim.*, 1955, Abstr. No. 14,251.—Chromotropic acid gives with solutions of nitrites a yellow colour, the intensity of which depends on the acidity and time after mixing. The mol. concn. of the reagent should be $\not< 5$ times that of the nitrite. The concn. of acid, H$_2$SO$_4$ or HCl, should be between N and 5 N. Beer's law is not obeyed. To detect NO$_2'$, 1 to 2 ml of the solution are mixed with 1 ml of 0·01 M reagent solution and 1 to 2 ml of 3 to 5 N mineral acid. In the presence of NO$_2'$ a yellow colour appears after 5 min., and its intensity increases with time. Ferro- and ferri-cyanides, CrO$_4''$ and Cr$_2$O$_7''$ interfere, but NO$_3'$ do not. As little as 5 μg of NO$_2'$ can be detected in 50 ml viewed through a 100-mm depth. To determine NO$_2'$, 25 ml of solution containing 0·05 to 0·2 mg are treated with 2 to 3 ml of 0·01 M reagent and 10 ml of 5 N H$_2$SO$_4$, the solution is diluted to 50 ml and the extinction is measured at 400 to 500 mμ with a blue filter after 2 hr. A calibration curve is obtained under the same conditions.   G. S. SMITH

1315. Spectrophotometric determination of phosphorus in vanadium pentoxide. L. Bloch and R. A. J. Thienpont. *Chem. Weekbl.*, 1955, **51** (52), 919–925.—Methods based on the pptn. of P as molybdophosphate are unsatisfactory, as it is difficult to avoid the formation of complexes of compounds of quinquevalent V with the molybdophosphate. Two methods are described for the prep. of a solution of the sample (commercial V$_2$O$_5$) for analysis by the proposed method. The sample (5 g or 2 g) is dissolved in 50 per cent. v/v H$_2$SO$_4$ (with or without the addition of HNO$_3$), the proportions being adjusted so that the concn. of H$_2$SO$_4$ in the final dilution (100 ml per g of the sample) shall be 2 N. In the course of this prep., the solvent acid is momentarily heated to fuming in order to ppt. the Si as SiO$_2$, and the refractory portion of the sample, after having been moistened with 50 per cent. H$_2$SO$_4$ and HF, is fused with KHSO$_4$ for a short time only, at the lowest possible temp. The method depends on the preliminary removal of V from this soln. (50 ml $\equiv$ 0·5 g of the sample) with the use of cupferron by a known method, removal of excess of cupferron by extraction with chloroform (3 $\times$ 10 ml) and the pptn. of the H$_3$PO$_4$ from the aq. phase (including a washing with 10 ml of 2 N H$_2$SO$_4$ from the chloroform phase) as ferric phosphate. This ppt. is filtered off, washed, and transferred, with the filter, to a beaker, the filter-paper being spread out evenly on the wall of the beaker. After washing down the bulk of the ppt. with warm water, the remainder of the ppt. is removed from the paper by washing down with 10 ml of 33 per cent. v/v HClO$_4$. The resulting soln. is filtered (if possible through the same filter-paper), and the filtrate (with washings) is analysed spectrophotometrically for its content of P by the known colorimetric method based on the formation of ammonium molybdovanadophosphate. A blank is prepared by similar treatment of an equal wt. of pure V$_2$O$_5$. A calibration curve, which is linear for a range of 50

to 700 μg of P, is prepared from results obtained with known amounts of pure V_2O_5. The reproducibility of results lies within ± 0.003 per cent. of P. The results are in good agreement with those obtained by standard methods. The accuracy of the method is not affected by the presence in the sample of 0·2 per cent. of As or 10 per cent. of Fe.

P. S. ARUP

1316. New method of determination of arsenic as pentasulphide. K. I. Kal'pchiev (Dimitrov Tech. Coll., Bulgaria). *Zh. Anal. Khim.*, 1955, **10** (5), 334.—The ppt. obtained with H_2S from strongly acid arsenic solutions always contains As_2S_3 and S. If the ppt. is dissolved in the minimum amount of nearly colourless ammonium sulphide solution, oxidation of As_2S_3 to As_2S_5 occurs. Treatment with HCl gives As_2S_5 and S which can be filtered off on a crucible and washed with carbon disulphide to give As_2S_5. This can be dried at 105° C and weighed.

G. S. SMITH

1317. Decomposition of arsenic sulphides by ammonium salts. P. M. Isakov and É. I. Korytkova. *Nauch. Byull. Leningrad. Univ.*, 1954, (32), 14–17; *Referativnyĭ Zh., Khim.*, 1955, Abstr. No. 11,865.—A finely ground sample of the arsenic mineral (orpiment) is placed in a flask with a rubber bung which carries a tube dipping into water in a beaker. A mixture (2:1) of NH_4Cl and NH_4NO_3 (50 times the wt. of sample) is shaken with the sample and the flask is heated on a hot-plate. Decomposition is completed within 5 to 6 min., as shown by the almost complete cessation of bubbling through the water. The contents of the flask, with As as $AsCl_3$ and S as SO_4'', and the water in the beaker are combined. Orpiment, but not arsenical pyrites, can be completely decomposed by NH_4NO_3 alone in 5 to 7 min. Arsenical pyrites is best decomposed by a mixture (1:10) of NH_4Cl and NH_4NO_3.

G. S. SMITH

1318. Rationalisation of the rhodamine-B method for antimony. R. W. Ramette and E. B. Sandell (Univ. of Minnesota, Minneapolis, Minn., U.S.A.). *Anal. Chim. Acta*, 1955, **13** (5), 455–458.—The photocolorimetric determination of micro amounts of Sb is based on the benzene extraction of rhodamine-B chloroantimonate formed in an acid aq. soln. of Sb^V (*cf.* Webster and Fairhall, *Brit. Abstr. C*, 1946, 77). The chemistry of the procedure and the sources of error are discussed; slight modifications for improving the accuracy are proposed. Extraction of the complex is more complete and the rate of hydrolysis is lower if the extraction is made from $3\ M$ HCl instead of $6\ M$. A rhodamine-B concn. of $2 \times 10^{-3}\ M$ is preferred.

W. J. BAKER

1319. Photometric determination of antimony in solders. E. I. Ishutchenko and V. M. Eliseeva. *Zavod. Lab.*, 1955, **21** (7), 791.—An application of the methyl violet method to the analysis of solders containing 1·5 to 2·5 per cent. of Sb is described. *Procedure*—The finely divided solder (0·1 g) is dissolved in 1 ml of conc. H_2SO_4, the cooled solution is heated with 10 ml of dil. HCl (1 + 1) to dissolve the salts and transferred to a 100-ml calibrated flask; 1 g of NaCl is added, and the solution is made up to the mark with dil. HCl (1 + 1). A 10-ml aliquot is diluted to 50 ml with dil. HCl (1 + 1) in a 50-ml calibrated flask, and 10 ml of this solution are treated with 10 per cent. $NaNO_2$ solution to oxidise Sb and, after 5 min., mixed with an equal vol. of water. Excess of $NaNO_2$ is destroyed by the addition of 0·5 ml of saturated urea solution, the

solution is diluted to 50 ml with water in a separating funnel and 10 drops of methyl violet solution (concn. not stated) and 20 ml of xylene or toluene are added. After extraction of the complex in the organic solvent, the aqueous solution is again extracted in a second funnel with 10 ml of the solvent. The colour intensity of the combined extracts is measured photometrically, with a red colour filter. A calibration curve is prepared from standards. No interference is given by Cu, Bi and As.

G. S. SMITH

1320. Polarographic titrations with a rotating platinum electrode. III. The determination of antimony in alloys with potassium dichromate. I. Bozsai (Rákosi Mátyás Iron and Metal Works, Budapest). *Magyar Kém. Foly.*, 1955, **61** (10), 305–308.—The method depends on oxidation of Sb^{III} to Sb^V with $K_2Cr_2O_7$, excess of which is titrated after 30 min. with $Fe^{..}$ soln. in a vol. of 100 ml in the presence of Knop's soln. [H_3PO_4 (d, 1·7; 150 ml) and H_2SO_4 (d, 1·8; 150 ml) diluted to 1 litre] (20 ml) and conc. HCl (10 ml) until the diffusion current suddenly increases. A rotating platinum electrode, kept at $+1·0$ V *vs.* the S.C.E., is used. If Ag is present, 2 per cent. acacia mucilage (5 ml) is added before the HCl. Volumes of 20 to 50 ml containing 5 to 10 mg of Sb are used for the titration. Arsenic must be pptd. previously as $MgNH_4AsO_4$. Antimony (10 μg) in a vol. of 100 ml can be determined with an accuracy of ± 6 per cent., but with larger amounts the accuracy is of the order of ± 1 per cent. The method can be used for the antimony content of bronzes, Babbitt metals, solders and metallurgical by-products. A few mg per cent. of Sb in copper alloys can be determined.

A. G. PETO

1321. Separation of antimony and arsenic by means of alizarin red S. V. L. Khukhiya and T. V. Areshidze (Caucasus Inst. Mineral Raw Materials). *Zavod. Lab.*, 1955, **21** (7), 785–787.—In the presence of Na_2SO_4 at pH 1·5 to 4·5, alizarin red S precipitates Sb but not As. The ppt. is insol. in 5 per cent. Na_2SO_4 solution acidified with H_2SO_4 and in 14 per cent. Na_2SO_4 solution; Bi, Pb, Hg, Sn, Ti and Zr are pptd. with Sb. Ferric iron is not pptd. but gives a dark-brown colour which interferes with the observation of indicators when neutralising the solution and when checking for completeness of pptn.; this effect is prevented by the addition of oxalate. *Procedure*—For the determination of Sb, not more than 100 ml of the solution in H_2SO_4 are treated with 0·2 to 0·4 g of oxalic acid and neutralised to methyl orange with NaOH solution (first 10 then 2 per cent.). Alizarin red S solution (0·5 per cent.) (15 to 30 ml) is stirred in over a period of 2 min. When pptn. is complete, the ppt. is filtered off after 10 to 15 min. and washed 6 or 7 times with 5 per cent. Na_2SO_4 solution acidified with H_2SO_4. It is then dissolved in hot water and the solution, about 100 ml, is boiled with 25 ml of conc. H_2SO_4 and successive additions of 0·1 N $KMnO_4$ until the liquid is decolorised. The solution is reduced with aq. SO_2 solution, added in small portions during 10 to 12 min., in the presence of 5 g of Na_2SO_4, then boiled for 15 min. to remove SO_2. Concentrated HCl (5 ml) is added to the hot solution and Sb is titrated with 0·01 N $KBrO_3$ to methyl orange. The As, present in the filtrate from the pptn. of Sb, can be determined with $KBrO_3$ after treatment with SO_2. The method is applicable to antimony ores and concentrates.

G. S. SMITH

1322. Co-precipitation in quantitative analysis. III. The co-precipitation of antimony with manganese dioxide with the use of radioactive indicators. A. K. Babko and M. I. Shtokalo (Inst. Gen. and Inorg. Chem., Acad. Sci. USSR). *Zavod. Lab.*, 1955, **21** (7), 767–773.—The radioactive isotope ^{124}Sb, with a half-life of 60 days, is used in a study of the co-pptn. of Sb with MnO_2. The pH range for complete separation of Sb with MnO_2 (from $MnSO_4$ and $KMnO_4$) is 1 to 7. Fluorides and other substances that form complexes with Sb hinder the pptn. A physicochemical method—the method of isomolar series—is suggested for studying the possible formation of compounds in co-pptn., and its applicability is confirmed in the system $Cr(OH)_3$-$Zn(OH)_2$. Solutions of chromite and zincate of equiv. molar concn. are mixed in various proportions so that the sum of the volumes remains constant. Included in the zincate solution is ^{65}Zn, with a half-life of 250 days, and each solution contains a small excess of NaOH. The solutions are boiled, the ppt. is filtered off and dissolved in HCl and the activity of the HCl solution is measured. The no. of counts per min. is plotted against the composition of the original solutions. With increasing content of Zn the no. of counts rises to a max. at 50 per cent. and then falls; the curve thus resembles the usual property diagram corresponding to the formation of a chemical compound at equimolar concn. In the MnO_2- Sb system the curve mounts steadily and shows no bend, indicating that there is no chemical interaction. By the method of radioactive indicators it is shown that the NaH_2PO_2- copper-foil method, as given in the GOST specification for determining Sb in metallic Cu, needs modification in that the washing of the copper foil on which Sb has been deposited results in loss of Sb. In most cases it is sufficient to ppt. Sb with MnO_2 and dissolve the ppt. for direct colorimetric determination in the solution. If the NaH_2PO_2- copper-foil process is desirable, the pptd. Sb should be dissolved in Na_2O_2 solution without being washed.

G. S. SMITH

1323. Vortmann and Metzl's method for the separation of antimony and tin. I. Sarudi (Chem. Res. Inst., Szeged, Hungary). *Z. anal. Chem.*, 1955, **148** (1), 21–25.—The separation of Sb and Sn by Vortmann and Metzl's method (*Z. anal. Chem.*, 1905, **44**, 525) was investigated to test its suitability for quant. analysis, and the reliability of the method was confirmed. The separation is sharp and is independent of the amount of either metal present. The black ppt. of Sb_2S_3 can be readily filtered off and dries without oxidation. The following procedure is given for the preparation of the soln. for separation. An alkali polysulphide soln. of the metals, after decolorisation with KCN, is evaporated to 10 ml, diluted to 30 ml and 5 to 10 ml of H_2SO_4 (5:1) are added. Most of the acid is removed by heating, leaving a moist residue of $Sb_2(SO_4)_3$ and $Sn(SO_4)_2$. To the cooled residue are added 10 ml of H_2O, the mixture is heated, with shaking, and the soln. is then allowed to stand in the cold with 10 ml of conc. HCl and 2 g of tartaric acid. The flask is warmed, with shaking, for 1 min. over a small flame, allowed to stand and then gently warmed after the addition of 10 ml of H_2O. The soln. is filtered into 15 ml of syrupy H_3PO_4, the flask being washed out with a total of 30 ml of HCl (1:2) and with one wash of 1 to 2 per cent. tartaric acid soln. After the filter has been washed with the tartaric acid soln., the filtrate is made up to 120 ml, when it is ready for the Vortmann and Metzl separation

by passing H_2S through at the temp. of a boiling-water bath. The Sb_2S_3 is filtered off whilst the soln. is still hot, and washed successively with cold water, alcohol ($\times$ 3), CS_2, alcohol, and ether. The crucible is dried at 110° C for 20 to 30 min. The Sn is best determined on the antimony-free filtrate after evaporation on a water bath with 1 g of NaCl to remove HCl. The Sn is pptd. with H_2S and the SnS_2 ignited to SnO_2.

J. H. WATON

1324. Analysis of an alloy of bismuth, lead and tin. I. P. Ryazanov and L. A. Molot. *Uch. Zap. Saratovsk. Univ.*, 1954, **34**, 211–213; *Referativnyĭ Zh., Khim.*, 1955, Abstr. No. 14,267.—Bismuth and Pb are separated from Sn by pptn. with Na_2S in an alkaline medium in the presence of potassium tartrate; Bi is determined as $BiPO_4$, Pb as $PbSO_4$ and Sn by electrolysis. *Procedure*—The alloy (0·3 g) is dissolved by heating on a sand bath for 10 to 15 min. with 15 ml of dil. HCl (1 + 1) and 5 ml of conc. HNO_3, 3 g of potassium tartrate are added and dissolved by heating, and the cooled solution is diluted to 100 ml. Potassium hydroxide (about 7·5 g) is added until the solution is alkaline to litmus, and a solution of 1 g of $Na_2S.9H_2O$ is added at once. The solution is diluted with warm water to 200 ml and heated for 30 min., after which it is set aside for 1·5 to 2 hr. The sulphide ppt. is filtered off and washed with 2 per cent. Na_2S solution. The filtrate is used for the electrolytic determination of Sn. The ppt. is dissolved on the filter in 50 ml of hot dil. HNO_3 (2 + 1) and the filter is washed free from Bi. The solution is evaporated to 50 ml, 5 ml of dil. H_2SO_4 (1 + 1) are added, and the Pb is determined as $PbSO_4$. The filtrate containing Bi is evaporated to 100 ml, and the Bi is determined as $BiPO_4$ in the usual way. The filtrate from the sulphide ppt. is evaporated to a vol. of 80 to 100 ml, heated with 1·5 ml of 30 per cent. H_2O_2 solution, cooled, made acid to litmus with $\simeq 2$ ml of conc. HCl, heated for 10 to 15 min. and then treated with 5 g of oxalic acid and 2·4 g of hydroxylamine hydrochloride. Tin is determined by electrolysis at 0·6 amp., 2·4 to 3 V and 70° C. A further 0·5 g of hydroxylamine hydrochloride is added after 1 hr. The Sn is deposited on a coppered-platinum electrode. Electrolysis of the stirred solution takes $\simeq 3$ hr. The deposit is washed with water and dried at 80° to 85° C.

G. S. SMITH

1325. Determination of vanadium by means of reducing volumetric solutions. I. Direct determination of vanadium with ascorbic acid. L. Erdey, E. Bodor and I. Buzás (Inst. Gen. Chem., Tech. Univ., Budapest). *Acta Chim. Acad. Sci. Hung.*, 1955, **7** (3–4), 277–285.—In the rapid method described the end-point of the titration is shown by Variamine blue. A solution containing 0·05 to 0·2 g of V_2O_5 is neutralised against phenolphthalein with N NaOH, then acidified with N H_2SO_4 (10 ml), and made up to 100 ml with water. This solution is titrated with 0·1 N ascorbic acid until the colour changes from brown through green to blue - green. A solution of Variamine blue (1 per cent.; 0·2 ml) is added, when the colour changes to dark violet, and titration is continued until the colour changes to pale blue. The end-point is confirmed by adding one drop of indicator to the solution. The titration must be completed in 3 min. The accuracy of the method is within ±0·5 per cent.

II. Indirect determination of vanadium with ascorbic acid. L. Erdey, I. Buzás and E. Bodor. *Ibid.*, 1955, **7** (3–4), 287–292.—A method is des-

cribed for the indirect determination of V^V by means of ascorbic acid and ferrous sulphate solution free from $Fe^{...}$. The titration is carried out quickly in cold solution slightly acidified with HCl. The endpoint is indicated by Variamine blue. A solution containing 0·1 to 0·2 g of V_2O_5 is neutralised with NaOH to phenolphthalein, N HCl (15 ml) and 0·1 N ferrous sulphate solution (5 ml) (from which $Fe^{...}$ have been removed by a cadmium reductor) are added and the solution is diluted to 100 ml with water. The solution is titrated with 0·1 N ascorbic acid as described above. The accuracy of the method is within $\pm 0·1$ per cent.

III. Determination of vanadium with a ferrous salt. L. Erdey, K. Vigh and E. Bodor. *Ibid.*, 1955, **7** (3–4), 293–305.—The method has been applied to the determination of vanadium in ferrovanadium, in steel, in vanadium pentoxide, and in vanadium mud. Ferric ions are bound by either H_3PO_4, NaF or $Na_4P_2O_7$. For the determination of the vanadium contents of chromium-containing steels, the samples are oxidised with $KBrO_3$, when only the vanadium is oxidised. *Procedure for vanadium pentoxide*—A sample (0·5 g) is dissolved in dilute H_2SO_4 (1 : 3; 10 ml) and the solution is made up to 100 ml with water. A 50-ml portion of this solution is added to 30 per cent. H_2O_2 (3 ml), and the excess of peroxide is destroyed by boiling for a few minutes. The cooled solution is treated with NH_4Cl (5 g) and 0·1 N $KBrO_3$ solution (25 ml) and boiled for 15 min. The solution is allowed to cool and $Na_4P_2O_7$ (4 g) is added. The resulting solution is titrated with 0·1 N $FeSO_4$ solution to Variamine blue.

C. A. SLATER

1326. X-ray spectrographic method for the determination of vanadium and nickel in residual fuels and charging stocks. E. N. Davis and B. C. Hoeck (Sinclair Res. Lab., Inc., Harvey, Ill., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1880–1884.—A rapid method is described for the X-ray spectrographic determination of trace quant. of Ni, Fe and V. The sample ($\simeq 20$ g) is first ashed, brought into soln. and evaporated on a sample plate and rotated under an X-ray beam. The intensity of the resulting fluorescent radiation from the sample is then determined. Counts recorded per sec. on a Geiger tube are a linear function of both Ni and V over the range 0 to 14 μg. To lessen the air absorption of X-rays of the order used for $VK\alpha$ 2·502 A and $VK\alpha$ 2·280 A, a helium gas path is arranged in line with the collimator of nickel-foil plates. The glass sample-plate (a 15-mm microscope coverglass), on which the final soln. of ash is evaporated, is positioned, at a point determined by expt., so that it receives the greatest intensity distribution and there rotated at $\simeq 30$ r.p.m.; rotation results in greater uniformity of counts per sec. D. G. HIGGS

1327. Iodine monochloride as a catalyst in reduction of quinquevalent vanadium by arsenous acid. G. S. Deshmukh and M. G. Bapat (Hindu Univ., Benares, India). *Z. anal. Chem.*, 1955, **148** (5), 347–349.—The reduction of V^V in HCl soln. by As^{III} is catalysed by ICl and the procedure may be used for the determination of V^V, since As^{III} is oxidised by BrO_3' in preference to V^{IV}. *Procedure*—A known excess of As_2O_3, followed by a little 0·005 M ICl, is added to V^V in HCl soln. and (after reduction is complete) the excess of As_2O_3 is titrated with $KBrO_3$ soln. Thus 0·02 to 0·085 g of V in 10 ml of soln. may be be determined with an accuracy within $\pm 0·5$ per cent. J. P. STERN

1328. Separations with a mercury electrode: determination of certain metallic impurities in vanadium salts. W. E. Schmidt and C. E. Bricker (Princeton Univ., New Jersey, U.S.A.). *J. Electrochem. Soc.*, 1955, **102** (11), 623–630.—Copper, Pb, Cd and Zn, in quantities as small as 10 μg, can be quant. removed by electrolysis from solutions as conc. as 0·5 M in V. The small quantities of non-passive metals (Cu, Pb, Cd, Zn) may then be removed by back electrolysis at controlled potentials and the passive metals (Fe, Co, Ni) by distillation of the mercury cathode after stripping. Subsequent estimation of the metals may be made by conventional polarographic or other methods.

S.C.I. ABSTR.

1329. Colorimetric determinations of low concentrations of oxygen in gases. C. Stafford, J. E. Puckett, M. D. Grimes and B. J. Heinrich (Phillips Petroleum Co., Bartlesville, Okla., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 2012–2014.—An apparatus and procedure are described for determining <100 p.p.m. of oxygen in nitrogen, butane, butadiene, ethylene, propylene, etc., by spectrophotometric measurement of the bleaching effect of the oxygen on the red colour of the reduced form of sodium anthraquinone-2-sulphonate. An improved form of Brady's apparatus (*Brit. Abstr. C*, 1949, 203) is used and is calibrated against known vol. of electrolytically generated oxygen. The error is ± 7 per cent. over the range of 10 to 50 p.p.m. of oxygen; six samples can be analysed in $\simeq 8$ hr. There is no interference by H, CO_2, other acidic gases, or C_2H_4, but high values are obtained if the concn. of CO in the sample is >15 times that of oxygen. The method is adaptable to continuous automatic instrumentation. W. J. BAKER

1330. Rapid mass-spectrometric micro-method of isotopic analysis of oxygen in water. A. I. Brodskiĭ, S. G. Demidenko, L. L. Strizhak and V. R. Lechekhleb (L. V. Pisarzhevskiĭ Inst. Phys. Chem. Acad. Sci. Ukr. SSR, Kiev). *Zh. Anal. Khim.*, 1955, **10** (4), 256–261.—A mass-spectrometric method for determining the isotope composition of oxygen in water with a 20-mg sample is described.

G. S. SMITH

1331. Use of vanadium pentoxide in combustion method for sulphur in refractory materials. D. B. Hagerman and R. A. Faust (Socony Mobil Lab., Paulsboro, N.J., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1970–1972.—A rapid method of determining total sulphur in certain inorganic sulphides and sulphates, cracking and reforming catalysts, etc., involves heating a mixture of the sample (0·3 to 0·6 g) and excess of V_2O_5 (1 g) in a quartz tube at 900° to 950° C, absorbing the liberated gases in 6 per cent. v/v H_2O_2 and titrating the resulting H_2SO_4 with 0·01 or 0·1 N NaOH. An addition of powdered $Cr_2O_3 \cdot Al_2O_3$ ($\equiv$ 20 to 30 per cent. of Cr) is necessary for sulphide samples. Acid-forming elements can interfere, but Ca, Ba, Na and Al do not. An analysis can be made in $\simeq 45$ min. and the error is $\nsucc 0·06$ per cent. for sulphur contents <5 per cent., or $\simeq 0·1$ per cent. for higher sulphur contents. The method is suitable also for suspensions of $BaSO_4$ or Ba sulphonate additives in oils. W. J. BAKER

1332. Continuous potentiometric determination of traces of hydrogen sulphide in hydrogen by absorption in iodine solution. F. Čůta and Z. Burianec (Vysoká Škola chem.-tech., Prague, Czechoslovakia). *Chem. Listy*, 1955, **49** (4), 503–509.—Hydrogen gas

containing traces of H_2S is passed through an absorber (illustrated) filled with a very dil. soln. of I, free from I'. By means of a calibration curve, the content of H_2S can be determined from the difference of the redox potentials of the absorbing soln. before and after absorption. With $10^{-4}\,N$ and $10^{-5}\,N$ soln. of I it is possible to determine, respectively, 0·5 to 0·02 mg and 0·05 to 0·003 mg of H_2S per litre with an error of ± 5 per cent. The method is suitable for the continuous control of purity of technical hydrogen. G. GLASER

1333. Paper-chromatographic separation of polythionic acids. E. Scoffone and E. Carini (Centro Studio Chim. Nucl., Padua, Italy). *Ric. Sci.*, 1955, **25** (7), 2109–2113.—Of a large number of solvent mixtures for the separation of tri-, tetra-, penta- and hexa-thionates on paper, the best separations were given by *n*-butanol - acetic acid - ethyl acetoacetate - H_2O (10 : 2 : 1 : 7), with R_F values of 0·20, 0·30, 0·48 and 0·60 for the tri-, tetra-, penta- and hexa-derivatives, respectively, and *n*-butanol - acetic acid - H_2O (4 : 1 : 5) (organic phase), with R_F values of 0·06, 0·10, 0·19 and 0·28. Development is continued for 12 hr., and the spots are detected with $AgNO_3$. T. P. McLAUGHLIN

1334. Photometric determination of chromium as perchromic acid in ethyl acetate solution. A. Glasner and M. Steinberg (Hebrew Univ., Jerusalem, Israel). *Anal. Chem.*, 1955, **27** (12), 2008–2009.—The chromium in aq. soln. at pH $1\cdot7 \pm 0\cdot2$ and 10° C is converted into blue perchromic acid, which is then extracted with ethyl acetate (three extractions are made) and determined spectrophotometrically at 580 mμ and $\not> 20°$ C. Large amounts of Fe, Mn, V, W and Mo do not interfere. This direct method ensures more complete recovery of Cr than does the diphenylcarbazide method in which only one extraction is made. Slightly low values are obtained on chrome-steels (containing 0·75 and 4·40 per cent. of Cr). W. J. BAKER

1335. Spectrophotometric titration of chromium and vanadium. J. W. Miles and D. T. Englis (Univ. Illinois, Urbana, Ill., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1996–1998.—Methods are given for the spectrophotometric titration at 350 mμ (150-ml quartz cell) of $Cr^{\cdots\cdots}$ with either 0·1 N $FeSO_4$ or arsenous acid in 5 N H_3PO_4, and of $V^{\cdots\cdots}$ with 0·1 N $FeSO_4$ in the presence of H_3PO_4. Solutions containing Cr and V can be oxidised with $KBrO_3$ and the $Cr^{\cdots\cdots}$ titrated spectrophotometrically at 350 mμ with 0·1 N arsenous acid, followed by the titration of $V^{\cdots\cdots}$ with 0·1 N $FeSO_4$. The dichromate titration proceeds rather slowly towards the end-point; good curves with sharp breaks at both end-points are obtained. For contents of Cr of 1·7 to 17·3 mg per 50 ml of soln. the error is $\simeq 0\cdot4$ per cent., whilst for contents of V of <5 mg per 50 ml it is 0·6 per cent. A procedure for steel samples containing these elements is given; the iron is removed (it absorbs strongly at 350 mμ) by pptg. the hydroxides of Cr and V with $NaHCO_3$. W. J. BAKER

1336. Polarographic behaviour of some elements in concentrated calcium chloride solution. V. Determination of chromium in the presence of nickel. J. S. Beveridge, G. F. Reynolds and H. I. Shalgosky (Min. Supply, Kidbrooke, London, England). *Anal. Chim. Acta*, 1955, **13** (5), 494–498.—An extension of previous studies (*Anal. Abstr.*, 1954, **1**, 27, 28 and 1210) on the polarography

of Ni and Cr in conc. aq. $CaCl_2$ at pH $\not> 3\cdot5$ and temp. of 90° to 100° C is reported. For the direct determination of Ni and Cr when present together (*e.g.*, in calcium metal), the combined Ni and Cr wave is obtained first in 5 M $CaCl_2$, as described previously. The Cr wave only can then be obtained in a $CaCl_2$ - hydroxylamine base electrolyte (adjusted to 7·4 M Cl' and 0·4 M NH_2OH) and the concn. of Ni and Cr can be calculated from calibration graphs. The concn. of each metal should preferably be from 6 to 60 μg per ml, with Ni : Cr $\not> 2$. W. J. BAKER

1337. The reaction of chromic complex compounds with ion-exchange resin. III. Exchange reactions between a cationic exchanger of styrene type and cationic complex ions of chromium. Yoshiyuki Inoue, Akira Kawamura, Keizo Wada and Hiroshi Okamura (Fac. Agric., Kyoto Univ., Kyoto, Japan). *Japan Analyst*, 1955, **4** (5), 277–280.—The ion-exchange reaction between $[Cr(H_2O)_6]^{\cdots}$ and $[Cr(H_2O)_4(Ox)_2]^{\cdot}$ (Ox = oxalate) and Amberlite IR-120 was studied in various salt forms of the resin and it was found that the exchange proceeds well when the resin is in the form of hydrogen, sodium and potassium salts. It was also found that the size of the network structure of the resin has a significant effect on the exchange with chromium complexes. Sulphonated polystyrene (**I**) exchanges with Cr complexes better than the usual IR-120 or 112, which contain a significant amcunt of divinylbenzene and thus have a smaller network structure. **I** also exchanges well with a soln. of cationic chromium complexes which has been subjected to partial hydrolysis or treatment with alkali.

IV. A systematic analysis of complex ions of chromium with sulphonated polystyrene and Amberlite IR-4B. *Ibid.*, 1955, **4** (5), 281–285.—A systematic separation of complex ions of Cr with various charges was studied with an ion-exchange resin. A mixed soln. of chromium complexes with different charges is passed through a column of **I**. Both the tervalent and univalent cationic complexes exchange quant. with **I**. Neither the tervalent nor non-electrolytic complex is adsorbed on **I**, but a significant amount of univalent anionic complex is adsorbed. The eluate is passed through a column of Amberlite IR-4B (acetate). Both uni- and ter-valent anionic complexes are quant. exchanged and only the non-electrolytic complex is found in the eluate. Both cationic and anionic univalent complexes on the column of **I** are eluted with 0·05 N $HClO_4$, whereas the tervalent cationic complex remains on the column and is eluted on the passage of >20 ml of N $HClO_4$ (for $\simeq 15$ mg of Cr). By passing the 0·05 N $HClO_4$ soln. through a column of IR-4B, the univalent anionic complex is adsorbed on the column and the univalent cationic complex is found in the eluate. The amount of Cr is determined in each fraction to give the amounts of complexes of different charges. This method can be applied to the study of ageing of chromium complexes, including chrome tanning materials obtained by the reduction of $K_2Cr_2O_7$ with various reducing agents. K. SAITO

1338. Separation of sexavalent molybdenum by paper chromatography. Qualitative and quantitative evaluation of chromatograms. G. Almássy and J. Straub (Inst. Med. Chem., Med. Univ., Debrecen, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1955, **7** (3–4), 253–257.—A solvent system is described with which Mo^{VI} can be separated from other metal ions, the R_F values being, for Mo^{VI}, 0·58, and for other

cations, 0·77 to 0·91. As little as 0·1 μg of Mo^{VI} can be detected in 0·1 ml of test solution. The test solution (not more than 0·1 ml) is spotted on filter-paper (Schleicher and Schüll No. 498). If no Fe^{III} is present in the solution, a 1 per cent. solution of Fe^{III} (0·1 ml) is added to the spot. The chromatogram is developed at 20° C, with a solvent consisting of 96 per cent. ethanol, conc. HCl and water (40 : 10 : 50, by vol.). When the solvent front has travelled to a distance of 15 cm, the paper strip is dried at 60° to 70° C and treated with a 5 per cent. solution of potassium ferrocyanide.

C. A. SLATER

1339. Determination of molybdenum by ion exchange and polarography. R. L. Pecsok and R. M. Parkhurst (Univ. California, Los Angeles, Calif., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1920–1923.—Molybdenum is determined, particularly in steels, by polarographic reduction of Mo^{VI} in 0·1 M H$_2$SO$_4$ - 0·5 M citric acid. Well-formed doublet waves are obtained for the reduction to Mo^V and Mo^{III}. Diffusion currents are directly proportional to concn., but slightly dependent on pH and ionic strength. All interfering cations are removed with Dowex 50-X12 cation-exchange resin. Procedures are given for preparing solutions when W is present.

D. G. HIGGS

1340. Colorimetric determination of molybdenum in tungsten-bearing steels. L. J. Wrangell, E. C. Bernam, D. F. Kuemmel and O. Perkins (Allis-Chalmers Mfg. Co., Milwaukee, Wis., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1966–1970.—A rapid method of determining from 0·25 to 9 per cent. of Mo in a wide variety of tungsten-containing steels is described. The sample (0·1 g) is dissolved in a mixture of HNO$_3$, HCl and H$_2$O (1 + 1 + 3); a mixture of H$_2$SO$_4$ and H$_3$PO$_4$ (1 + 1) is then added, followed by heating to fumes of SO$_2$. The thiocyanate colour is developed in the diluted soln. of the residue after suitable adjustments. Interference by the yellow thiocyanate complex of tungsten is avoided by using a green filter in the photometer. A minimum correction factor for Cr is substituted for the usual volatilisation of this element. The orange-coloured thiocyanate complex of Mo$^{·····}$ is stabilised with 2-butoxyethanol and its absorbance is measured at 525 mμ in a 1-cm cell. The readings are referred to standard calibration curves, from which the correction for Cr is also calculated. The standard deviation is ±0·015, and one sample can be analysed in ≃1 hr. The presence of W or of <5 per cent. of Co does not affect the results. The accuracy is equal to that of the longer peroxide - H$_2$SO$_4$ and titrimetric methods.

W. J. BAKER

1341. Molybdenum determination in soils and rocks with dithiol. L. J. Clark and J. H. Axley (Univ. Maryland, College Park, Md., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 2000–2003.—A spectrophotometric procedure for the accurate determination of 0·02 to 10 μg of Mo in rocks, soils, sewage sludges, inorganic fertilisers, etc., is described fully. The sample (2 g) is fused with Na$_2$CO$_3$ (4 g) in a platinum crucible, the SiO$_2$ is removed from the HCl soln. of the melt, and the filtrate is diluted to 100 ml so as to contain ≃6 ml of conc. HCl. A 25-ml aliquot of this soln. is adjusted to 4 N HCl, Fe$^{···}$ are removed by reduction with KI and the iodine is decolorised with Na$_2$S$_2$O$_3$; 1 ml of tartaric acid is added, to sequester any W, followed by 2 ml of 0·2 per cent. dithiol soln. to develop (in ≃10 min.) the green molybdenum - dithiol complex. The

complex is then extracted with *iso*amyl acetate (5 ml) and, after ≃30 min., its extinction is measured at 680 mμ in a Coleman Junior spectrophotometer, fitted with cells 12 mm × 75 mm. The colour is stable almost indefinitely; the content of Mo is calculated from standard curves and is corrected for the reagent blank. The precision is 0·02 μg per g of sample. Tin and ≯100 μg of Cu or As do not interfere; >10 μg of Pt or 100 μg of Rh gives high results.

W. J. BAKER

1342. Aromatic amines as reagents for tungsten. F. Lucena-Conde and J. Zato (Univ. Salamanca, Spain). *An. Real. Soc. Esp. Fís. Quím.*, 1955, **51B** (11), 605–612.—4 : 4′-Diamino- and 4 : 4′-diamino-3 : 3′-dimethyldiphenylmethane are unsuitable as precipitants for W owing to the solubility of the ppt., but 4 : 4′-diaminotriphenylmethane is satisfactory. Under suitable additions the pptn. with this reagent is quant. and the effect of pH on the solubility of the base and on the pptn., and of the temp. of pptn. have been examined. The ppt. has a variable composition, ≃ 4WO$_3$.C$_{19}$H$_{18}$N$_2$.xH$_2$O, and must be ignited (at 700° to 900° C) to WO$_3$ for gravimetric determination. Alternatively the ppt. may be treated with an excess of aq. NaOH, and the excess of alkali titrated with acid. The reagent also precipitates Mo and V, but not quant., and PO$_4$$^{′′′}$ in the presence of W. It may also be used to test for oxidising agents, giving a dark-green colour, *e.g.*, with Ce$^{····}$, MnO$_4$$^{′′′′}$ or Cr$_2$O$_7$$^{′′}$, but is unsuitable as a volumetric redox indicator.   L. A. O'NEILL

1343. Polarographic determination of small amounts of tungsten in ores. D. L. Love (Pennsylvania State Univ., University Park, Pa., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1918–1920.—A method is described for the determination of W in low-grade ores resulting from the extraction of molybdenite from granitic ore, the tungsten minerals present being wolframite and hubnerite. The expected range of tungsten content was 0·001 to 0·10 per cent.; a preliminary separation of the W was effected by extracting interfering substances with conc. HNO$_3$ and then the W with conc. HCl. The W is determined polarographically in constant-boiling HCl as the supporting electrolyte. Oxygen is removed by N satd. with HCl. Filtration through sintered glass is necessary since attack by HCl on cellulose results in additional waves near that of W.

D. G. HIGGS

1344. Colorimetric micro-determination of sexavalent uranium with morin. G. Almássy, Z. Nagy and J. Straub (Inst. Exp. Physics, L. Kossuth Univ., Debrecen, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1955, **7** (3–4), 317–323.—In the method described, interfering ions may be complexed with EDTA (disodium salt) if they occur in only small concentrations. In larger concentrations use is made of the solubility of uranyl nitrate in ether to remove it from the interfering ions. *Procedure*— About 18 ml of neutral soln. containing 50 to 400 μg of uranium are measured into a 25-ml flask. To this soln. are added N HCl (0·5 ml), 25 per cent. aq. NH$_4$Cl soln. (2 ml), EDTA (disodium salt) soln. (1·5 per cent.; 2 ml), and ethanolic morin soln. (0·33 per cent.; 0·6 ml). The soln. is allowed to stand for 5 min. and aq. NH$_3$ (sp. gr. 0·880) (1 ml) is added and the soln. is made up to volume with water. The intensity of colour is measured, after 10 min., in a Pulfrich photometer, with filter S47 and 2-cm cuvettes. The colour is stable for 30 min.

C. A. SLATER

1345. Determination of uranium in iron. L. Kosta (J. Stefan Inst., Ljubljana, Yugoslavia). *Rep. J. Stefan Inst., Ljubljana*, 1955, **2**, 7–8.—To determine U in concn. of 0·0001 to 0·001 per cent. in ferrous metals by extracting the U from a nitrate solution with ethyl acetate and then preparing fluorescent discs (*cf. Slov. Acad. Sci. Arts Rep.*, 1953, **1**, 12), a preliminary concn. is necessary to remove Fe, Mn and V, which quench the fluorescence. The metal (2 g) is dissolved in hot $HClO_4$ which is diluted to 1 M and electrolysed for 2 hr. at 4 amp. between a platinum anode and mercury cathode (c.d. 0·3 amp. per sq. cm). Aluminium (20 mg), as nitrate, is dissolved in the electrolyte now free from interfering metals, and pptd. by aq. NH_3. The $Al(OH)_3$ and co-pptd. U are dissolved in 5 ml of 2 N HNO_3 and the extraction procedure is applied to this solution. A 90 to 95 per cent. recovery is obtained. A. R. PEARSON

1346. Coulometric titration of uranium with electrogenerated titanous ion. J. J. Lingane and R. T. Iwamoto (Harvard Univ., Cambridge, Mass., U.S.A.). *Anal. Chim. Acta*, 1955, **13** (5), 465–472.—Sexavalent uranium ($UO_2^{··}$) can be titrated coulometrically with $Ti^{···}$ generated by reduction of 0·08 M $Ti^{····}$ at a mercury-pool cathode, the anode being a cadmium rod and the indicator electrode bright-platinum foil. The titration is made at 85° C in 75 ml of soln., containing 0·25 to 1 M citrate, adjusted to a pH of 0·5 to 1·5, the equivalence point (e.p.) being determined accurately with a potentiometer. By using a const. generation-current and time to the e.p., the mean error for 28 to 112 mg of U is −0·02 per cent. Elements reducible by $Ti^{···}$ must be removed from the soln. The titration cell and procedure are described fully. The supporting electrolyte is prepared from pure $TiCl_4$. W. J. BAKER

1347. Combined radiometric and fluorescent X-ray spectrographic method of analysing for uranium and thorium. W. J. Campbell and H. F. Carl (U.S. Bureau of Mines, College Park, Md., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1884–1886.—The sample, of −325 mesh, assumed to be in a state of equilibrium, is placed in suitable containers and packed to a given level by means of a spatula; the container is positioned at a pre-determined distance from the Geiger-counter window. The radioactivity is measured as counts per min. above background, usually over a period of 8 min. By comparison with calibration curves obtained from radioactive standards, the "per cent. equiv. U" is obtained. The sample is next placed in the fluorescent X-ray spectrograph to determine the ratio Th : U and, as a first approximation, the line-intensity equation—$Th_{L\alpha}/U_{L\alpha} = C$ (wt. per cent. Th/wt. per cent. U)—applies, where C is determined for a particular set of conditions from samples of known Th and U content. The Th and U content is then calculated from given equations. The method is independent of mineral type or matrix of the sample and the lower limit of detection is 0·01 to 0·03 per cent. of U or Th. The time required for both elements is $\simeq 20$ min. D. G. HIGGS

1348. Simplified high-temperature sampling and use of pH for solubility determinations. System uranium trioxide - sulphuric acid - water. W. L. Marshall (Nat. Lab., Oak Ridge, Tenn., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1923–1927.—Solubility curves for $UO_3.H_2O$ in aq. H_2SO_4 (1·0 to 0·00023 M) between 150° and 290° C have been determined by directly sampling a soln. equilibrated with solid $UO_3.H_2O$ at the desired temp. and then comparing the pH of the separated sample at 25° ± 0·04° C with control pH data. The pressure-bomb and assembly described and illustrated enables an equilibrated soln. to be sampled periodically with speed and ease without any withdrawal of solid-phase particles. The pH values are obtained by the use of a vibrating-reed electrometer coupled to a potentiometer and recorder; they are accurate to ±0·002 to 0·004 pH unit. The solubility data obtained are expressed empirically in terms of temp. and molarity of UO_3 and H_2SO_4. W. J. BAKER

1349. Gravimetric determination of fluorides. T. I. Badeeva (N.G. Chernyshevskii Saratov State Univ.). *Zavod. Lab.*, 1955, **21** (7), 787–788.—An application of the method of Clark *et al.* (*Analyst*, 1932, **57**, 138) is described. G. S. SMITH

1350. Rapid titrimetric determination of microgram amounts of fluoride ion with SPADNS - thorium lake. G. Banerjee (Darjeeling Gov. Coll., Darjeeling, India). *Anal. Chim. Acta*, 1955, **13** (5), 409–414.—From 1 to 100 μg of F' in 50 ml of soln. (pH 3, sodium acetate - HCl buffer) can be quickly titrated with 0·004 M aq. $Th(NO_3)_4$, with 1 ml of 0·02 per cent. aq. SPADNS (*cf. Anal. Abstr.*, 1956, **3**, 74) as indicator. The titration is continued until the final colour (blue - violet) matches a blank containing a buffered soln. of the indicator plus 0·05 ml of the $Th(NO_3)_4$ soln. If ions that form complexes with Th are present, the fluoride must be separated, *e.g.*, as SiF_4, by distillation. The accuracy of the method is very high, the end-point being quite sharp. W. J. BAKER

1351. Polarometric determination of fluorine in soluble fluorides with ferric chloride. K. Kadič and Z. Řezáč (Spolek pro Chem. a Hutní Výrobu, Ústí n. Lab., Czechoslovakia). *Chem. Listy*, 1955, **49** (4), 570–572.—A polarographic method for the determination of F' at 0·0 V by titration with $FeCl_3$, according to the equation $6F' + Fe^{···} \rightleftharpoons [FeF_6]'''$, is described. The soln. containing $\simeq 25$ mg of F' in 25 ml of H_2O at pH 5 to 7 is treated with an equal vol. of ethanol and a large excess of solid NaCl ($\simeq 8$ g), and titrated with $FeCl_3$ while CO_2 is passed in. Before reading the galvanometer, stirring is stopped and CO_2 is passed over the soln. The average error of 17 determinations was −0·12 per cent. Sulphate ions in amounts >10 mg interfere. Fluorosilicates must first be decomposed by treating the boiling soln. with N NaOH until red to phenolphthalein. G. GLASER

1352. Determination of halogens in organic substances. I. Determination of chlorine, bromine and iodine. P. N. Fedoseev and M. Ya. Sobko (S.O. Makarov Nikolayev Ship-building Inst. USSR). *Zh. Anal. Khim.*, 1955, **10** (5), 323–326.—The material is ignited in a rapid stream of oxygen (150 to 200 ml per min.) at 800° to 900° C without a catalyst, and the products of combustion pass through a horizontal tube filled with small crystals of KI and then into an absorption tube containing 10 per cent. KI solution. The tube containing solid KI acts as a filter, holding back the fumes which otherwise would not be completely absorbed on passing through the liquid absorbent. Chlorine compounds on combustion give Cl and HCl, and bromine and iodine compounds give Br and I only. To determine Cl, the contents of the two tubes of

KI are washed into a flask, 10 to 20 ml of $0.05 N$ potassium hydrogen di-iodate are added and the liberated I is titrated with $0.05 N$ $Na_2S_2O_3$; Br and I are determined similarly but without the use of di-iodate. The time taken is 55 to 60 min. and the error is ± 0.2 per cent.   G. S. Smith

1353. Mercuro-reductimetric determination of hypobromite. V. M. Tarayan and E. N. Ovsepyan. *Nauch. Tr. Erevansk. Univ.*, 1954, **44**, 77–86; *Referativnÿi Zh., Khim.*, 1955, Abstr. No. 14,264.— Bivalent Hg readily reduces bromine and BrO′, but the reduction of BrO_3' is not quant. In the presence of Hg^{II}, bromine and BrO′ are reduced but BrO_3' is not reduced unless excess of Br′ is added. In titrating with mercurous nitrate solution a mixture of bromine and BrO′, the end-point is the appearance of a cloudiness due to Hg_2Br_2. Chloride and bromide do not interfere. Loss of bromine is prevented by the carrying out of the titration in a flask with a rubber stopper.
                    G. S. Smith

1354. Rapid method of determining iodide in iodised common salt. A. S. Shvets. *Gigiena i Sanit.*, 1954, (7), 41–43; *Referativnÿi Zh., Khim.*, 1955, Abstr. No. 14,265.—A filtered solution (100 ml) of 100 g of iodised salt in 500 ml of water is mixed with 4 ml of $0.1 N$ KOH or NaOH and 1 ml of satd. bromine water in a 250-ml flask with a ground-glass stopper. The solution is then mixed with 1 ml of N HCl and 5 to 10 drops of 5 per cent. phenol solution, and 1 ml of H_3PO_4 (sp. gr. 1.6 to 1.7) is added to form a complex with Fe^{III}. After the addition of 4 ml of KI soln. (5 per cent.) the stoppered flask is left in the dark for 3 min. and the solution is titrated with $0.005 N$ $Na_2S_2O_3$ in the presence of starch.   G. S. Smith

1355. Mercuro-reductimetric determination of manganese. V. M. Tarayan. *Nauch. Tr. Erevansk. Univ.*, 1954, **44**, 65–75; *Referativnÿi Zh., Khim.*, 1955, Abstr. No. 14,230.—In N H_2SO_4, $KMnO_4$ is quant. reduced to Mn^{II} by $Hg_2(NO_3)_2$ solution and can be determined potentiometrically without interference from Cr^{VI} and V^V. A visual titration can be carried out in the presence of $AuCl_3$ as catalyst (1 drop of $0.03 N$ in 50 to 80 ml); and in $3 N$ H_2SO_4 under these conditions fairly large amounts of $KMnO_4$ can be determined. Mercurous nitrate solution is added until the violet colour of $KMnO_4$ is replaced by a yellow - brown colour, the solution is then shaken carefully for 2 to 3 min., the violet colour returns, and the titrant is then added very slowly in drops until the violet colour disappears. In $5 N$ H_2SO_4 the valency of the Mn in the reduced solution has a value between 3.2 and 3.6.   G. S. Smith

1356. Polarographic determination of manganese and iron. M. Pleva (Ústav keram., Brno, Czechoslovakia). *Chem. Listy*, 1955, **49** (2), 262–264.— Manganese and Fe in triethanolamine give well-developed and reproducible waves, suitable for analytical purposes. Applying this method to the determination of Mn and Fe in cements and slags, it has been found that the addition of EDTA suppresses interference by the large excess of Ca and Mg present. Further, the addition of starch catalyses the decomposition of H_2O_2 formed during the oxidation of Fe and Mn by oxygen in the air, and thus appreciably reduces the waiting period before the polarography proper. To determine Fe_2O_3 in cements and slags, evaporate the sample (0.25 g)

with a mixture of H_2SO_4 $(1 + 1)$ (1 ml) and 40 per cent. HF (5 ml), dissolve the residue in HCl $(1 + 20)$ and dilute the soln. to 50 ml with the same solvent. To an aliquot (5 ml) add a saturated soln. of EDTA (disodium salt) (7 ml), a saturated soln. of triethanolamine hydrochloride (2 ml), NaOH soln. ($\simeq 50$ per cent.) (2 ml) and starch soln. (2 per cent.) (0.5 ml). Shake the mixture well and, after 1 hr., bubble H through the soln. and polarograph from 0.6 to 1.2 V. The same procedure is followed for the simultaneous determination of MnO and Fe_2O_3, the Mn wave being registered from 0.0 to 0.5 V.
                    G. Glaser

1357. Analytical chemistry of rhenium. D. I. Ryabchikov and A. I. Lazarev (V. I. Vernadskiĭ Inst. Geochem. and Anal. Chem. Acad. Sci., USSR, Moscow). *Zh. Anal. Khim.*, 1955, **10** (4), 228–235. —In the colorimetric determination of Re with thiourea, the solution is mixed with 5 ml of conc. HCl, 5 ml of 5 per cent. aq. thiourea solution and 1 ml of 20 per cent. $SnCl_2$ in HCl and diluted to 25 ml with water in a calibrated flask. After 5 to 10 min. at $65°$ to $75°$ C, the solution is cooled and the colour intensity is measured, with a deep-blue filter; 10 to 15 μg of Re can be determined in 25 ml. Oxidising agents, $Hg^{..}$, Cd, Bi, Mo, W, Te, Se, As, and ions that form stable complexes with thiourea, interfere. Fluorides, citrates, tartrates and oxalates do not interfere, and the interference of Sb can be masked by F′. Another determination is based on the reaction of Re with diphenylthiourea, when a ppt. of the composition

$$\left[ReO_2 \left(S = C \overset{NH-C_6H_5}{\underset{NH-C_6H_5}{\diagdown}} \right)_4 \right] Cl$$
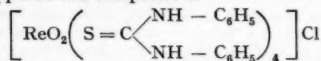
is obtained. The ppt. is dissolved in NaOH and H_2O_2, and the thiocyanate colorimetric method is applied.   G. S. Smith

1358. Micro-crystalloscopic reaction for bivalent iron with 2-nitroindane-1 : 3-dione. M. Matskanova, V. Oshkaya and G. Vanag. *Izv. Akad. Nauk Latv. SSR*, 1954, (5), 113–114; *Referativnÿi Zh., Khim.*, 1955, Abstr. No. 14,236.—A drop of $< 0.05 N$ Fe^{II} solution mixed with a drop of 6.5 per cent. (saturated) 2-nitroindane-1 : 3-dione soln. gives a violet colour and, after 2 to 3 min., violet - black long hexagonal tablets of the ferrous compound. The minimum amount of Fe detectable is 1.5 μg, and the limiting dilution is 1 in 6600. Larger crystals form in an acid medium. Silver, Pb and Cu give yellow cryst. ppt., and Co an orange ppt., but other cations are not pptd. No interference is caused by SO_4'', Cl′, NO_3', F′, BO_3''', ClO_3', acetate, formate, oxalate, lactate, tartrate, succinate and other anions. Very large amounts of I′ and Br′ interfere because of the formation of dark complex salts.   G. S. Smith

1359. The application of standard methyl orange solution in micro-analysis: helianthometry. Helianthometric micro-determination of ferrous iron and hydrogen peroxide. G. Almássy and I. Dezső (Med. Univ. of Debrecen, Hungary). *Magyar Kém. Foly.*, 1955, **61** (10), 300–305.—Chromate ions oxidise methyl orange (I), in the presence of oxalate and ferric ions and light, in a buffered acid soln., to a colourless product. The reaction is carried out in u.v. light, as the consumption of I depends on the light intensity. The method is also used for the determination of reducing agents. The equiv. wt. of I depends on the vol. of the original soln.

and on the concn. of Fe^{III}. *Procedure*—A soln. of $FeCl_3.6H_2O$ is prepared by dissolving 5 g in conc. HCl (10 ml) and diluting to 100 ml with H_2O. For the determination of Fe^{II}, the soln. (1 to 5 ml), $\not> 0.1$ N acid, is added to a mixture of 0·001 N $K_2Cr_2O_7$ (1 ml) and conc. H_3PO_4 (sp. gr. 1·7; 0·5 ml) and the soln. is diluted to 6·5 ml.; the oxidation requires 1 min. Ferric chloride soln. (0·1 ml), 10 per cent. Na_2CO_3 (1 ml) and saturated Na oxalate (0·5 ml) are added. The soln. is immediately titrated with 0·001 per cent. I soln. by adding 0·5-ml portions and, after each addition, holding the soln. near (20 to 30 cm) to a u.v. lamp until the colour turns green; after the end-point, it remains red. A second, accurate titration is carried out similarly, but the last 0·5 ml is added dropwise. In a blank, the $Fe^{..}$ soln. is replaced by H_2O. The sensitivity is 1 μg of Fe^{II} per ml. The following do not interfere: $Ca^{..}$, $Mg^{..}$, $Ni^{..}$, $Cd^{..}$, $Zn^{..}$, $Al^{...}$, $Cu^{..}$, $Fe^{...}$, $Co^{..}$, alkali metals, Cl′, SO_4'', PO_4''' and NO_3'. For the determination of H_2O_2, to a mixture of 0·001 N $K_2Cr_2O_7$ (1 ml) and conc. H_3PO_4 (sp. gr. 1·7; 0·5 ml) the unknown soln. (0·5 to 5 ml, acidity $\not> 0.1$ N) is added and then diluted to 6·5 ml with H_2O. After 15 min., the three reagents are added (as above) and the soln. is titrated as before. The same ions, except $Fe^{...}$, do not interfere. The sensitivity is 0·3 μg of H_2O_2 per ml. **A. G. Peto**

1360. Determination of iron in iron ores and agglomerates by means of EDTA (disodium salt). Yu. I. Usatenko and L. I. Mikhaĭlova (Dnepropetrovsk Chem.-Tech. Inst.). *Zavod. Lab.*, 1955, **21** (10), 1168–1169.—The powdered ore (0·1 g) is moistened with water and dissolved in HCl. Insoluble materials are first fused with Na_2CO_3. The acid solution is neutralised with aq. NH_3, 1 or 2 drops of conc. HCl are added to dissolve any ppt., the solution is diluted to 100 ml, 3 drops of 20 per cent. sulphosalicylic acid are added, and the solution is titrated with EDTA (disodium salt) solution (18·613 g per litre) until the reddish-violet colour turns to lemon yellow. Sulphosalicylic acid gives a clearer end-point than does KSCN.

G. S. Smith

1361. Potentiometric determination of iron in products from the treatment of nickel. S. E. Kreĭmer. *Zavod. Lab.*, 1955, **21** (7), 788–790.—The method is based on the reduction of $Fe^{...}$ with $Na_2S_2O_3$ in the presence of $Cu^{..}$. The indicator electrode is a rotating platinum wire and the reference electrode is a mercurous iodide electrode with an agar - KCl bridge. With Ni, 1 g is dissolved in the minimum amount of dil. HNO_3 (3 + 2), the solution is evaporated to a syrup, 50 ml of water are added, the solution is heated to dissolve salts, then cooled, and 10 ml of 10 per cent. $CuSO_4$ solution are added. The acid is neutralised with 15 per cent. NaOH solution, any cloudiness is removed by the addition of dil. HNO_3 (1 + 10), and 10 to 15 drops are added in excess. The rotating electrode is inserted, the reference electrode is connected, and the solution is titrated potentiometrically with 0·02 or 0·1 N $Na_2S_2O_3$. With solutions containing Fe, oxidation with HNO_3 is essential. No interference is given by Al, Co, Cu, Cl′ and SO_4''; Pd should be absent. **G. S. Smith**

1362. Differential amperometric titration of iron and vanadium. I. P. Alimarin and S. I. Terin (M. V. Lomonosova Inst. Fine Chem. Tech.). *Zavod. Lab.*, 1955, **21** (7), 777–779.—At +0·9 V, Fe^{II} but not V^{IV} gives an anodic diffusion current. With the addition of Ce^{IV} the current falls in proportion to the amount of Fe^{II} oxidised and becomes zero when all the Fe^{II} is oxidised. If the potential is now changed to +0·5 V, the current is practically unchanged but, on further addition of Ce^{IV}, V^{IV} becomes oxidised and a cathodic diffusion current appears. The titration curve allows both Fe and V to be determined. **G. S. Smith**

1363. Determination of contents of iron and zinc in acid zinc electrolytes. I. N. Lekhovitskiĭ (Kharkov Electrotech. Works). *Zavod. Lab.*, 1955, **21** (10), 1172–1173.—In acid zinc baths, Fe is present in the ferrous state only. After addition of dil. H_2SO_4, direct titration with 0·1 N $KMnO_4$ gives the iron content. The solution after titration is boiled with HCl, cooled, and titrated for Zn in an aliquot portion with 0·2 N $K_4Fe(CN)_6$ containing $K_3Fe(CN)_6$, with $Na_4P_2O_7$ to combine with the Fe, and diphenylamine as indicator. **G. S. Smith**

1364. Method for separating α- and γ-ferric oxides. R. Schrader (Tech. Hochsch., Dresden, Germany). *Z. anal. Chem.*, 1955, **148** (5), 339–346.—Irrespective of particle size, the stable hexagonal $α$-Fe_2O_3 can be separated quant. (within 1 per cent.) from the metastable magnetic $γ$-Fe_2O_3 by dissolution of the $γ$-Fe_2O_3 in 2 per cent. HF at 20° C. Other acids are less effective than HF and the method described permits the isolation of 1 to 2 per cent. of the $α$-oxide, present in $γ$-Fe_2O_3 as impurity, dissolution of the $γ$-oxide being complete within 30 min. **J. P. Stern**

1365. Amperometric titration of ferrocyanide and phosphate by vanadyl salts. V. L. Zolotavin and V. K. Kuznetsova (S.M. Kirov Ural Polytechnic Inst.). *Zavod. Lab.*, 1955, **21** (11), 1283–1284.—In 0·1 N H_2SO_4 the solubility of vanadyl ferrocyanide is 9.3×10^{-5} mole per litre. In 0·1 N KCl the solubility of vanadyl phosphate is 0.62×10^{-5} mole per litre (temp. not stated). Ferrocyanides can be determined amperometrically in 0·1 N H_2SO_4 with the dropping-mercury electrode at 1·0 V *vs.* the S.C.E. by titration with vanadyl sulphate solution. Phosphates can be determined similarly in 0·1 N KCl if a sodium acetate buffer solution is added to maintain the neutrality of the solution during the addition of vanadyl sulphate solution, which is normally of pH 2 to 2·5. **G. S. Smith**

1366. Spectrographic determination of residual elements in steel. Spectrographic Analysis Sub-Committee of B.I.S.R.A. (Metallurgy Div., B.I.S.R.A., 11 Park Lane, London, England). *J. Iron Steel Inst.*, 1955, **181** (4), 316–318.—A method for the spectrographic determination of V, Mo, Co, Sn and Ti in steel, with a low-voltage intermittent-arc source unit, is described. The effect of silver and graphite counter-electrodes was studied and it was observed that the density of the Ni and Co lines was enhanced when silver electrodes were substituted for graphite, although the overall intensity of the Fe spectrum diminished.

S.C.I. Abstr.

1367. Determination of free and carbide carbon in austenitic chrome - nickel steel. N. M. Popova and L. V. Zaslavskaya. *Zavod. Lab.*, 1955, **21** (11), 1285–1288.—The amount of free C in a 20 - 20 chrome - nickel steel can be determined by anodic dissolution of the steel, treatment of the carbide ppt. with H_2O_2, which oxidises the free carbon, and

obtaining the difference between the contents of total and combined plus graphitic carbon. Amorphous carbon adsorbs bromothymol blue in an amount dependent on its concn. in a mixture with carbon. A method based on this observation is proposed for determining free carbon in steel. The free carbon in anodic ppt. from austenite and martensite shows similar adsorption properties. (An editorial note to the paper indicates that the evidence for the validity of the adsorption method is not yet sufficient.)　　　　　　　G. S. SMITH

1368. **Spectrographic method of determining magnesium in spheroidal cast iron.** Z. Czajkówna. *Przeglad Odlewnictwa*, 1955, **5**, 46–50.—Magnesium (0·03 to 0·5 per cent.) is determined in spheroidal cast iron with an accuracy of ±13 per cent. by the use of a quartz spectrograph with medium dispersion and graphite electrodes (each 6 mm in diameter and 15 mm long), 4 mm apart. Dissolve 2 g of cast iron in HCl, oxidise with HNO$_3$ and dilute to 100 ml. Place one drop of this soln. on the bottom electrode, dry in air and apply 15,000 V to form a spark. Measure photographically the intensities of the following spectrum lines: Mg 2802·7 and Fe 2767·5 A. Compare their intensities with standard soln. containing Fe and different amounts of Mg.　　　　　　　CHEM. ABSTR.

1369. **An improved barium sulphate method for the determination of sulphur in steel.** B. Bagshawe and A. L. Pill (The Brown - Firth Res. Lab., Sheffield, England). *Analyst*, 1955, **80**, 796–802.—A critical review of the conventional barium sulphate method for S in steel (B.S. 1121: Part 1: 1943) showed that the method although reasonably but not entirely satisfactory for simple carbon steels is much less so for alloy chromium steels. The error occurs in co-pptn. of S with basic compounds of Cr formed during the removal of NO$_3$′ by baking. In the modified procedure described, the baking treatment is replaced by treatment with hydroxylamine hydrochloride to decompose residual NO$_3$′. This procedure is applicable to steels of all ranges of Cr content and to all highly alloyed steels, with the exception of those of high Ti content. The precision of the method is within 0·002 per cent.　　　　　　　A. O. JONES

1370. **The determination of sulphur in plain carbon steel.** R. Belcher, D. Gibbons and T. S. West (The University, Birmingham, England). *Analyst*, 1955, **80**, 751–754.—The sample is dissolved in HCl and HNO$_3$, the soln. is evaporated to dryness and the residue is baked. In specified conditions of acidity the Fe is extracted with *iso*amyl acetate, the separated acid layer is evaporated to dryness and the residue is baked to remove Si. The residue is dissolved in HCl and treated with BaCl$_2$ soln. The washed ppt. is dissolved in a known excess of 0·02 *M* EDTA (disodium salt) and the excess is back-titrated with 0·01 *M* MgCl$_2$ soln., Solochrome black being used as indicator.　　　　　　　A. O. JONES

1371. **Analytical properties of xanthates. III. Colorimetric determination of cobalt as the ethylxanthate complex.** A. T. Pilinenko and N. V. Ul'ko (Kiev State Univ.). *Zh. Anal. Khim.*, 1955, **10** (5), 299–304.—The solubilities of various metal ethylxanthates in organic solvents are studied. The composition of the cobalt compound is Co(C$_2$H$_5$OCS$_2$)$_2$; it gives a deep-green solution in CCl$_4$, the colour intensity of which can be used for the determination of Co. *Determination of Co in iron - nickel ores*—A 0·05 to 0·1-g sample of the ore containing from 0·03 to 1 mg of Co is boiled with 5 to 10 ml of aqua regia, the solution is evaporated to fumes with 2 to 3 ml of dil. H$_2$SO$_4$ (1 + 4), the residue is extracted with water and the filtrate from the SiO$_2$ is collected in a separating funnel. Dilute HCl (1 + 1) (1 ml) is added and the ethylxanthates are pptd. by the addition of *M* K ethylxanthate. The ppt. is dissolved by shaking the solution with 10 ml of CCl$_4$, the CCl$_4$ layer is transferred to another funnel and shaken energetically with 20 to 30 ml of aq. NH$_3$ (1 + 1) containing ammonium tartrate (amount not stated), and the CCl$_4$ layer containing the Co, free from Ni and Fe, is separated and its colour intensity is measured by means of a photocolorimeter. The cobalt content is found from a calibration curve. *Determination of Co in steel*— The steel (0·05 to 0·1 g) is dissolved in conc. HCl with the subsequent addition of HNO$_3$, the solution is evaporated to dryness, the residue is moistened with HCl, dissolved in water and treated as described above.　　　　　　　G. S. SMITH

1372. **Separation of small amounts of nickel from cobalt by extracting nickel salicylaldimine.** I. P. Alimarin and V. V. Koreneva (M.V. Lomonosova Inst. Fine Chem. Tech., Moscow). *Zavod. Lab.*, 1955, **21** (8), 907–910.—Salicylaldehyde in the presence of aq. NH$_3$ and NH$_4$Cl gives with Ni·· the complex nickel salicylaldimine, which can be extracted with chloroform from aq. solutions; Be, Ti, V, Zr, La, Mn, Fe, Co··, Ni, Cu, Ca, Pb, Ce, Pr, Nb, Er, Th and U are also extracted, but Co··· are not extracted. Chloroform dissolves 0·034 mg of Ni in the complex form per 1 ml. *Procedure*— The solution, containing 0·01 to 0·1 mg of nickel, is treated with 2 ml of 4 *N* NH$_4$Cl, 0·5 ml of 2 per cent. alcoholic salicylaldehyde, and 20 per cent. aq. NH$_3$ to give a pH of 7·5 to 9·9. The solution is diluted with water to 10 ml and extracted with 10 ml of chloroform for 1 or 2 min. The chloroform layer is removed and the Ni extracted with dil. HCl (1 + 10); the solution is evaporated with HNO$_3$ and HCl to destroy the reagent and Ni is determined photocolorimetrically. In the presence of amounts of Co up to 100 mg in 10 to 20 ml, 1·5 ml of 100-vol. H$_2$O$_2$ are added after the aq. NH$_3$. The max. ratio of Co to Ni is 20,000:1. The method is applicable to the analysis of metallic cobalt, and cobalt ores and salts.　　　　　　　G. S. SMITH

1373. **Determination of [nickel in] electrolytic baths by a potentiometric method with EDTA (disodium salt).** L. Ya. Polyak. *Zavod. Lab.*, 1955, **21** (11), 1300–1301.—To determine Ni in nickel-plating baths, 20 ml of a 10 per cent. dilution of the electrolyte are neutralised with 10 per cent. NaOH solution and dil. H$_2$SO$_4$ (1 + 5), then mixed with 5 ml of 10 per cent. ammonium or sodium acetate and 40 ml of 0·1 *N* EDTA (disodium salt). With a platinum indicator electrode and a saturated calomel reference electrode the solution is titrated potentiometrically with 0·1 *N* FeCl$_3$. The Cu in copper baths, Zn in zinc baths and Cd in cadmium baths can be determined similarly.　　　　　　　G. S. SMITH

1374. **Solubility of dimethylglyoxime and of nickel dimethylglyoxime in ethanol - water mixtures.** A. K. Babko and P. B. Mikhel'son (Kiev State Univ., Ukrain. SSR). *Ukr. Khim. Zh.*, 1955, **21** (3), 388–393.—The solubility at 20° to 22° C of dimethylglyoxime rises gradually from 4·4 to 26 millimoles per litre as the ethanol content rises

from 0 to 48 per cent. v/v, and then abruptly to 121 millimoles per litre in 96 per cent. ethanol; over the same range the solubility of the nickel salt rises from 3 to 21 millimoles per litre, but becomes negligible in the presence of excess of dimethylglyoxime. The solubility of dimethylglyoxime in a series of organic solvents at 20° to 22° C is: CCl_4 0·7, xylene 3·5, benzene 3·8, toluene 4·2, $CHCl_3$ 4·6, dichloroethane 8·4, *iso*butyl alcohol 441, *iso*amyl alcohol 520, *n*-butanol 649 and ethanol 1148 mg per 100 ml. The partition coefficients of dimethylglyoxime between organic solvents and water are: *iso*butyl alcohol 8, *iso*amyl alcohol 9 and *n*-butanol 12.   R. TRUSCOE

1375. Analysis of nickel alloys used for oxide cathodes. I. Determination of magnesium. W. Noddack, G. Eckert and K. Riedel (State Res. Inst. Geochem., Bamberg, Germany). *Z. anal. Chem.*, 1955, **147** (6), 417–426.—For the estimation of Mg in nickel-alloy cathodes the Ni, together with Fe, Co, Mn, Cu, Cd, Pb and Zn, is quant. extracted by shaking with diethyldithiocarbamic acid (**I**) in $CHCl_3$. Magnesium and Al remain quant. in the aq. layer. After destroying any **I** in the soln., the Mg is determined colorimetrically with Titan yellow. The effect of Al is eliminated with EDTA (disodium salt) and that of small variable amounts of Ca by the addition of excess of $CaCl_2$ soln. *Procedure*—Enough sample to contain 5 to 20 μg of Mg is weighed into a 50-ml beaker and dissolved in HNO_3 (1:1); the soln. is twice evaporated to dryness with a little conc. HCl. After the residue has been dissolved in H_2O, the soln. is transferred to a 50 to 100-ml calibrated separating funnel and brought to a pH of 3 to 5 with 2 N NaOH and dil. HCl soln. The vol. of soln. should be $\simeq$ 15 ml. The heavy metals are extracted by shaking with 15 ml of a $CHCl_3$ soln. of **I**, followed by a further 3 to 4 extractions with 10 ml of reagent until the $CHCl_3$ layer is colourless. For amounts of Ni > 100 mg, the soln. should be divided into equal parts containing 100 mg or less, each part extracted separately with the reagent and the aq. layers combined. To destroy excess of reagent, the aq. soln. is transferred to a 100-ml beaker, acidified by the dropwise addition of 20 per cent. H_2SO_4 soln. and heated on a sand-bath until the soln. clears. After being cooled, the soln. is transferred to a 50-ml standard flask, diluted to 30 ml, and the following soln. are added in the order given—1 ml of a 10 per cent. glycerol soln., 2 ml of a 2 per cent. $CaCl_2$ soln., 2 ml of a 2 per cent. aq. soln. of EDTA (disodium salt), 0·4 ml of a 0·05 per cent. aq. soln. of Titan yellow and 5 ml of 2 N NaOH. The soln. is allowed to stand for 10 min. and the vol. is made up to 50 ml. The extinction is then measured and the content of Mg is obtained from a calibration curve, or the soln. can be compared visually with standard soln. The sensitivity of the method is 5 μg of Mg in the 50 ml of soln., which corresponds to 0·005 per cent. of Mg in a 100-mg sample. The average deviation for a content of Mg of 0·01 to 0·1 per cent. is $\simeq$ ±6 per cent. The **I** reagent is prepared by mixing 25 ml of an 8 per cent. soln. (v/v) of CS_2 in $CHCl_3$ with 25 ml of a 14 per cent. soln. (v/v) of diethylamine in $CHCl_3$ and diluting to 200 ml with $CHCl_3$. It should be stored in a brown bottle.

II. Determination of manganese. G. Eckert (Röhrenfabrik Siemens & Halske A.-G., Munich, Germany). *Z. anal. Chem.*, 1955, **148** (1), 14–20.—The Mn can be displaced quant. and selectively from other diethyldithiocarbamates by shaking with an aq. soln. of a zinc salt; traces of Fe may also be extracted if a large amount of Fe is present. The Mn is determined photometrically in the presence of the excess of Zn as its formaldoxime complex. *Procedure*—Enough sample to contain 5 to 25 μg of Mn is dissolved in the min. vol. of 50 per cent. HNO_3 soln., and the soln. is evaporated to dryness with 1 ml of HCl. The residue is dissolved in water and the soln. is extracted with a $CHCl_3$ soln. of diethyldithiocarbamic acid as described above. The $CHCl_3$ extract is twice shaken for 5 min. with 10 ml of 10 per cent. Zn acetate soln. and 2 ml of ammonium acetate buffer (470 ml of 15 N aq. NH_3 and 430 ml of glacial acetic acid made up to 1 litre). The combined aq. extracts are boiled with 1 ml of 2 M tartaric acid, cooled and treated with conc. aq. NH_3 until all the $Zn(OH)_2$ has redissolved. The soln. is transferred to a 50-ml flask, and the following reagents are added in the order given— 2 ml of 10 per cent. KCN soln., 1 ml of 1 per cent. hydroxylamine hydrochloride soln., 2 ml of formaldoxime soln. (10 g of paraformaldehyde and 22 g of hydroxylamine hydrochloride shaken with 100 ml of water and gently warmed until a clear colourless soln. is obtained) and 5 ml of conc. aq. NH_3. The soln. is made up to 50 ml, allowed to stand for 5 min., and its extinction is measured relative to that of a Zn acetate soln. to which the same reagents have been added. A Lange colorimeter with a BG5 filter is used for the determination. A mean error of ±5 per cent. is found for manganese contents of 0·005 to 0·1 per cent. on samples of 100 to 20 mg.   J. H. WATON

1376. Colorimetric determination of palladium with α-furildioxime. O. Menis and T. C. Rains (Nat. Lab., Oak Ridge, Tenn., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1932–1934.—Concn. of Pd as low as 0·1 p.p.m. can be determined spectrophotometrically to within 1 per cent. by measuring the extinction, at 420 mμ in the aq. phase, or 380 mμ in the $CHCl_3$ extract, of the yellow complex of Pd with a large excess of α-furildioxime in dil. HCl (0·1 to 1·4 N). In the aq. phase in the presence of 10 per cent. ethanol the coloured complex is stable for 20 min., and from 1 to 5 μg or less of Pd can be determined in 5-cm cells. In the $CHCl_3$ phase the colour is stable for at least 24 hr. Neither Pt, Ru, Rh, Ir nor Au interferes unless present as chloride, in which case these and other coloured ions should be eliminated by extracting the complex with $CHCl_3$. Except for CN', large amounts of anions do not interfere.   W. J. BAKER

1377. The volumetric assay of some binary alloys of palladium. R. H. Atkinson, R. N. Rhoda and R. G. Lomell (International Nickel Co., Inc., Bayonne, N.J., U.S.A.). *Analyst*, 1955, **80**, 838–839.—In the rapid method previously described for the assay of Pd - Ru alloys (Atkinson, *Anal. Abstr.*, 1954, **1**, 2420) the alloy was dissolved in the minimum amount of aqua regia. An alternative method that requires more aqua regia is now described. The alloy (0·15 g) is dissolved in 3 ml of conc. HCl, 3 ml of water and 0·6 ml of HNO_3 and the soln. is evaporated nearly to dryness. The residue is dissolved in 6 ml of dil. HCl (1 + 1) and the soln. is diluted to 100 ml. Aliquots (10 ml) of this soln. are treated with 5 ml of conc. HCl and 15 ml of 20 per cent. $FeSO_4$ soln. and are then titrated with 0·01 N KI soln. For Pd - Ag alloys solution is effected as described, but when the soln. is diluted to 100 ml enough conc. HCl is included to keep AgCl in solution. The titre then includes the Ag and Pd. Another aliquot is treated with a

slight excess of aq. NH_3, the excess is removed by boiling and, after further dilution, the liquid is cooled in ice and titrated with the KI soln. This titre corresponds to the Ag content. By comparison with a gravimetric method the method described is shown to be accurate to within $\pm 2\cdot 5$ parts per thousand for all alloys of Pd examined, with the possible exception of Pd - W alloys.

G. A. O. Jones

1378. Polarographic determination of platinum on solid electrodes. I. M. B. Bardin and Yu. S. Lyalikov (Kishinev State Univ.). *Zh. Anal. Khim.*, 1955, **10** (5), 305–309.—With platinum electrodes, $PtCl_4$ in $0\cdot 1$ N $NaNO_3$ gives two waves with $E_{\frac{1}{2}}$ of $-0\cdot 85$ and $-1\cdot 65$ V. The diffusion current in each case is proportional to the concn.

G. S. Smith

1379. The separation and quantitative determination of platinum, palladium, rhodium and iridium on paper strips. N. F. Kember and R. A. Wells (Chemical Res. Lab., Teddington, Middlesex, England). *Analyst*, 1955, **80**, 735–751.—Chromatographic methods are described for the separation of Pt, Pd, Rh and Ir in microgram amounts on paper strips. The chromatograms, prepared by downward diffusion of solvent, are developed in pairs, one being used for location of the metals by spraying with reagents. The corresponding fractions of the other strip are then extracted with the appropriate solvent, the extracts are treated with reagents and the metals (except Ir) are determined spectrophotometrically. Iridium is determined by microtitration with quinol soln. Satisfactory analyses of mixtures of all four metals containing large amounts of base metals have been made.

A. O. Jones

1380. Acid cupola slags. New method of rapid analysis. V. Williams. *Iron & Steel*, 1955, **28** (12), 525–526.—Details are given of a method for determining SiO_2, MnO, FeO, TiO_2, Al_2O_3, CaO and MgO in acid cupola slags. A $0\cdot 5$-g sample of finely powdered slag is intimately mixed with Na_2CO_3 and fusion is carried out, first over a Bunsen flame and then in an electric muffle-furnace at 900° C for 15 min. The product is cooled, 30 ml of conc. HCl and approx. 100 ml of hot water are added, and the fused cake is then dissolved by heating. Any residue is filtered off and the filtrate is evaporated to dryness. The constituents of the slag are determined as follows: SiO_2, by pptn., ignition and weighing; MnO, FeO and TiO_2, by Spekker photoelectric absorptiometer, blanks being obtained and the percentages read from a previously prepared graph; Al_2O_3, by pptn., ignition and weighing; from this weight the calculated weights of Fe_2O_3, TiO_2 and Mn_3O_4 are subtracted to obtain Al_2O_3; CaO and MgO, by titration with EDTA (disodium salt). With this method two persons can analyse 8 cupola slags per day.

G. C. Jones

1381. Conductimetric titration of exchange cations in clays. Z. P. Yakusheva. *Uch. Zap. Kazakhsk. Univ.*, 1954, **16**, 35–41; *Referativnyĭ Zh., Khim.*, 1955, Abstr. No. 14,269.—The clay ($0\cdot 5$ g) and 50 ml of water are placed in a beaker with a cover carrying a stirrer, two platinised-platinum electrodes and a burette. The electrical conductivity of the solution is measured after each addition of a standard HCl solution from the burette, and the conductivity is plotted against the vol. used. As the $H\cdot$ replace the cations in the clay the conductivity slowly increases, but when re-placement is complete the conductivity rises rapidly.

G. S. Smith

1382. The chemical analysis of a potassium oxide - lead oxide - silica glass, described as Standard Glass No. 3. Chemical Analysis Committee of the Society of Glass Technology (Hallam Gate Road, Sheffield, England). *J. Soc. Glass Tech.*, 1955, **39** (189), 57P–66P.—Detailed methods of analysis for SiO_2, PbO, Al_2O_3, CaO, MgO, K_2O, Na_2O, As, Fe and TiO_2 and loss on ignition are given. Boric oxide was determined by the method of Ball and Fajans (*Brit. Abstr. C*, 1952, 91). Mean values and standard deviations are given for a number of results obtained by different analysts using the methods on one sample of lead crystal glass.

N. E.

See also Abstracts 1423, 1424, 1425, 1426, 1441, 1442, 1501, 1548, 1549, 1560, 1563, 1578, 1583, 1589.

3.—ORGANIC ANALYSIS

1383. The micro-determination of carbon and hydrogen in organic compounds containing phosphorus. R. Belcher, J. E. Fildes and A. J. Nutten (Univ. Birmingham, England). *Anal. Chim. Acta*, 1955, **13** (5), 431–436.—When using the slow, catalytic micro-combustion method of Friedrich (*Brit. Abstr. A*, 1932, 71) for phosphorus-containing organic compounds, low values for C and high values for H can be avoided by covering the weighed sample in the platinum boat with 5 to 8 times its wt. of dried, ignited WO_3, and placing a porcelain boat filled with WO_3 just in front of the platinum foil and over the end of the furnace under the silica combustion-tube. This ensures complete absorption of phosphorus oxides; the filling should be renewed every 6 to 8 determinations. The modified Friedrich apparatus and procedure used are described in full.

W. J. Baker

1384. Use of silver permanganate in analysis. III. The determination of carbon and hydrogen with a short column of catalyst in the combustion tube. J. Körbl (Pharm. and Biochem. Res. Inst., Prague, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1955, **20** (5), 1026–1031.—The use of a catalyst prepared by the thermal decomposition of $AgMnO_4$ (*cf. Anal. Abstr.*, 1956, **3**, 733) is described. The combustion tube can be shortened to about a half of the normal length, a low combustion temperature (450° to 500° C) is employed, and the whole analysis is performed in 1 hr., the H_2O and CO_2 being absorbed in conventional Pregl absorption tubes. The capacity of the catalyst for S, Cl and I was found to be about 80 mg, 100 mg and 210 mg, respectively, whilst the capacity for Br is thought to be intermediate between that for Cl and I. Compounds containing F give high results for both C and H. When $\simeq 15$-mg samples are used, an accuracy better than that attainable by conventional methods is claimed.

P. S. Stross

1385. The micro-determination of carbon and hydrogen. Nickel as a reducing agent for nitrogen oxides. G. Kainz and F. Schöller (II Chem. Lab., Vienna Univ., Austria). *Z. anal. Chem.*, 1955, **148** (1), 6–9.—Nickel is superior to Cu as a means of reducing nitrogen oxides in the micro-determination of C and H. A layer of spongy Ni, 7 cm in length, suffices for 15 to 20 analyses, after which it is

regenerated by reduction in H. The relatively high m.p. of the Ni avoids any appreciable sintering during the determination. J. H. WATON

1386. Improvements in isotopic carbon assay and chemical analysis of organic compounds by dry combustion. D. R. Christman, N. E. Day, P. R. Hansell and R. C. Anderson (Brookhaven Nat. Lab., Upton, Long Island, N.Y., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1935–1939.—Modifications in the apparatus and combustion procedures (*cf.* Anderson *et al.*, *Brit. Abstr. C*, 1953, 14), by which micro samples of organic compounds are burned to CO_2 and water, are described. Improvements were made in the combustion-tube filling and its arrangement, the removal of nitrogen oxides, the trap and manometer system and the procedure for assaying ^{14}C. G. P. COOK

1387. A study of the accuracy obtained in Van Slyke combustion and radioassay of carbon-14 compounds. C. J. Collins and G. A. Ropp (Oak Ridge Nat. Lab., Tenn., U.S.A.). *J. Amer. Chem. Soc.*, 1955, **77**, 4160.—It has been shown that the procedure for measuring specific activities of carbon-14 compounds (Neville, *J. Amer. Chem. Soc.*, 1948, **70**, 3501) has an accuracy within ± 0·5 per cent. C. A. SLATER

1388. Determination of carbon and hydrogen in spontaneously flammable gases. H. B. Bradley (Linde Air Products Co., Tonawanda, N.Y., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 2021–2022.—A combustion technique is described for the determination of C and H in silane-containing gas mixtures or in any gas mixture in which there is a danger of explosion. The apparatus enables successive small portions of the gas sample to be mixed with a large excess of O and to be burned without uncontrolled explosions, which might rupture the combustion tube. Good results were obtained with gases containing silane and ethylsilane. G. P. COOK

1389. Determination of nitrogen in organic compounds by the Kjeldahl method. V. I. Esafov (Ural State Univ.). *Zavod. Lab.*, 1955, **21** (10), 1160–1163.—The decomposition of organic compounds is effected in a 150-ml round-bottomed flask fitted by means of a ground-glass connection to a small absorption tube with bulbs containing water. After the decomposition, the contents of the tube are combined with the main solution for the distillation with KOH solution. The addition of zinc filings to the H_2SO_4 - $KHSO_4$ mixture for decomposition is recommended in many cases. Conditions for obtaining accurate results with certain classes of compounds are described. *Amines, amides, phenylurethanes, aminonitro, nitro and azo compounds*—The sample (0·02 to 0·04 g) is dissolved in 1 ml of conc. H_2SO_4, 1 g of $KHSO_4$ is added and then 0·25 to 0·5 g of zinc filings, and the liquid is heated at 120° to 130° C for 1 hr., followed by stronger heating until decomposition is complete. *Heterocyclic azo compounds with one nitrogen atom in the ring*—The amount of $KHSO_4$ is increased to 4 g, the flask is heated for 2 hr. at 100° to 105° C, then for 2 hr. at 150° C, followed by 1 hr. at 250° C and finally at strong heat for complete decomposition. *Phenylhydrazones and phenylosazones*—The sample (0·01 to 0·02 g) is dissolved in 2 ml (3 ml for osazones) of conc. H_2SO_4 and treated with 0·25 g of glucose (0·5 g for osazones) and 2 g of $KHSO_4$. After 2 hr. at 100° to 105° C, the liquid is heated strongly to complete decomposition. *Heterocyclic*

azo compounds with two nitrogen atoms in the ring— The sample is heated with 3 ml of conc. H_2SO_4 alone for 4 hr. at 150° C; 0·5 g of glucose and 2 g of $KHSO_4$ are added and heating is carried to complete decomposition. G. S. SMITH

1390. Semi-micro determination of fluorine, chlorine and nitrogen in organic compounds. II. The use of cation-exchange resins. R. E. Banks, F. Cuthbertson and W. K. R. Musgrave (Durham Univ., England). *Anal. Chim. Acta*, 1955, **13** (5), 442–448.—The sample ($\equiv$ 10 mg of F, Cl and N) is fused in a nickel bomb with excess of Na at 600° to 700° C, as described by Belcher *et al.* (*Anal. Abstr.*, 1954, **1**, 492). An apparatus for destroying the excess of Na in an atm. of N at room temp. is described and illustrated. If no O is present in the sample, the N is determined, in 25 ml of the fusion soln., as CN′ by Denigès's method (*Compt. Rend.*, 1893, **117**, 1078). In another 25-ml aliquot, CN′ are destroyed with 0·1 M aq. formaldehyde and the total Cl′ and F′ are then determined by passing the soln. through a cation-exchange column (18 cm, 20 g of Amberlite IR-120), eluting for $\simeq$10 min. with water, and titrating the eluate (after boiling and cooling) with 0·02 N NaOH, with methyl red - methylene blue as indicator. The chloride in the same or a separate eluate is determined by titration with 0·01 N AgNO$_3$, with dichloro-R-fluorescein as indicator, or (for Cl′ concn. $\not\geq$ 1 mg per 10 ml) by treatment with mercuric hydroxycyanide (*cf. Anal. Abstr.*, 1954, **1**, 2696). If F′ are absent, CN′, CNO′ and absorbed CO_2 can be removed simply by boiling the eluate from the ion-exchange column. Precautions to be taken are stated. W. J. BAKER

1391. Mass-spectrometric method of analysis of chlorine derivatives of methane. S. E. Kupriyanov, R. V. Dzhagatspanyan, M. V. Tikhomirov and N. N. Tunitskiĭ (L. Ya. Karpov Sci. Res. Physicochem. Inst.). *Zavod. Lab.*, 1955, **21** (10), 1182–1188.—Methods for the analysis of mixtures of methane, chloromethane, dichloromethane, chloroform and carbon tetrachloride are described. G. S. SMITH

1392. Determination of tetrabromoethane, dibromoethane and dichloroethane in air. A. A. Belyakov (Gorki Inst. Hyg. Work). *Zavod. Lab.*, 1955, **21** (7), 796–798.—The sample of air is passed at the rate of 5 to 8 litres an hr. for at least 1 hr. through two absorption tubes containing 2·5 to 5 ml of 96 per cent. ethanol. To determine tetrabromoethane, 2·5 ml of the ethanol solution are mixed with 2·5 ml of 30 per cent. aq. KOH, and 2·5 litres of air (5 to 7 litres an hr.) are passed through the solution and then through two absorption tubes containing 5 ml of Ilosvay's reagent. The colour of the copper acetylide solution so obtained is examined photometrically, with colour filters 436 and 574 mμ. From 0·025 to 1 mg of tetrabromoethane in 5 ml of solution can be determined in 45 min. with an average accuracy of ±6 per cent. Acetylene is not absorbed by ethanol. To determine dibromo- and dichloro-ethanes, 2 ml of the ethanol solution are treated with 4 and 8 ml, respectively, of saturated ethanolic KOH. The solution is in an absorption tube joined with rubber tubing to an empty absorption tube and both outlets are closed by rubber tubing and glass stoppers. The tube containing the solution is heated on a boiling-water bath for 5 min. (for dibromoethane) or 20 min. (for dichloroethane). The vessel is cooled and 0·5 litre of pure air is passed through and then into

four wash-bottles containing in all 25 ml of Ilosvay's reagent. The solution is examined photometrically under the conditions named above. From 0·02 to 1 mg of either compound in 25 ml of solution can be determined in 30 to 45 min. with an accuracy of ±10 per cent. 　　　　　G. S. SMITH

1393. Cerate oxidimetry. III. Oxidation of glycerol, glycol and other organic compounds. N. N. Sharma and R. C. Mehrotra (Univ. Allahabad and Lucknow, India). *Anal. Chim. Acta*, 1955, **13** (5), 419–423.—Formic acid can be quant. determined by oxidation with $Ce(SO_4)_2$ only, provided that a few drops of 1 per cent. aq. $Cr_2(SO_4)_3$ are present to catalyse the reaction. Glycol and glycerol can be quant. oxidised with excess of $Ce(SO_4)_2$, either to formic acid (in $\simeq$ 30 min.) or to $CO_2 + H_2O$ (in $\simeq$ 70 min.) in the presence of conc. H_2SO_4 and 1 drop of 1 per cent. aq. $Cr_2(SO_4)_3$. By titrating the excess of $Ce(SO_4)_2$ (against $Fe^{..}$) in separate samples, after each of these two oxidation stages, a quant. determination of glycol and glycerol in a mixture can be made. In the procedures, 2 ml of glycol or glycerol, or a mixture of both, are refluxed with 5 to 10 ml of 0·1275 N aq. $Ce(SO_4)_2$ and 7 to 12 ml of conc. H_2SO_4. 　　W. J. BAKER

1394. Determination of aldehydes using unsymmetrical dimethylhydrazine. S. Siggia and C. R. Stahl (Gen. Aniline & Film Corp., Easton, Pa., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1975–1977.—An excess of unsymmetrical dimethylhydrazine solution is added to a sample and, after the reaction is complete, the excess of reagent is titrated with standard acid. Aromatic but not aliphatic aldehydes can be determined in the presence of ketones, and acetals and carboxylic acids do not interfere. The precision and recovery are within ±1 per cent. Satisfactory results were obtained with the 13 aldehydes analysed. 　　　　　G. P. COOK

1395. The paper-chromatographic analysis of aldehydes and ketones. II. The quantitative evaluation of aldehyde and ketone paper-chromatograms. K. E. Schulte and C. B. Storp. *Fette u. Seifen*, 1955, **57** (8), 600–604.—The spots on aldehyde and ketone paper-chromatograms are developed with a suitable reagent (Schiff's, Horrock's, Nessler's, 2:4-dinitrophenylhydrazine or *p*-nitrophenylhydrazine) and the intensity of the colour produced is measured at intervals along the spot and over its entire width by means of a photoelectric colorimeter; the area under the curve obtained by plotting intensity against distance along the spot is proportional to the amount of aldehyde or ketone present. The method can be applied to spots that overlap. An increase in sensitivity is achieved by carrying out the intensity measurements on a photographic negative or positive of the chromatogram; with constant experimental conditions highly reproducible results are obtained. 　　　　　E. HAYES

1396. Polarographic behaviour of monohaloacetones. Analysis of mixtures. P. J. Elving and R. E. Van Atta (Pennsylvania State Univ., University Park, Pa., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1908–1913.—Iodoacetone (**I**), bromoacetone (**II**) and chloroacetone (**III**) each show a single reduction wave over the pH range 1·5 to 10; the reductions are irreversible and diffusion-controlled. A 0·5 M acetic acid - sodium acetate buffer (pH 4·6) is employed as the supporting electrolyte and the value of $E_\frac{1}{2}$ is quoted as **I** $-0·14$ V, **II** $-0·35$ V

and **III** $-1·15$ V. The relative error involved in the simultaneous polarographic determination of the three haloacetones is <2 per cent. 　D. G. HIGGS

1397. Polarography of carbonyl compounds in methanol. W. Rogers, jun., and S. M. Kipnes (Temple Univ., Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1916–1918.—Well-defined waves are reported, for α- and β-dicarbonyls and for simple carbonyl compounds conjugated with a double bond, for both 0·3 M tetraethylammonium bromide (**I**) and 0·3 M LiCl (**II**) soln. in methanol. Maxima occurred only with diacetyl and pyruvic acid; these two substances produced only single waves, in contrast to their behaviour in buffered aq. media. Neither *n*-butyraldehyde nor acetonylacetone showed reduction waves below the decomp. potentials of **I** ($-2·2$ V) and **II** ($-2·1$ V). The $E_\frac{1}{2}$ for the first wave, if more than one wave is present, is reported as—benzil ($-0·53$ V), acetylbenzoyl ($+0·60$ V) and diacetyl ($+0·74$ V), and for the dicarbonyls, dibenzoylmethane ($-1·02$ V), benzoylacetone ($-1·22$ V) and acetylacetone ($-1·52$ V). The effect of increasing the separation of the carbonyl groups is reflected in the more negative potential of acetylacetone as compared with diacetyl and finally in the complete failure to reduce acetylacetone. 　　　　　D. G. HIGGS

1398. Determination of a carbonyl compound by extraction of its 2:4-dinitrophenylhydrazone. P. E. Toren and B. J. Heinrich (Phillips Petroleum Co., Bartlesville, Okla., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1986–1988.—A method for the determination of the butadiene - furfuraldehyde condensation product [2:3-4:5-di(but-2-enylene)tetrahydrofurfuraldehyde], a carbonyl compound used as a fly repellent, is described. It is based on the reaction of the compound with 2:4-dinitrophenylhydrazine in a two-phase system consisting of *iso*octane and an ethanol - water - phosphoric acid mixture. The hydrazone is extracted into the *iso*octane phase and its concn. is determined by the absorption at 340 mμ. Maximum sensitivity is claimed for a concentration of 5×10^{-6} M. 　　G. P. COOK

1399. Colour reactions of unsaturated carbonyl compounds. II. *p*-Aminodimethylaniline as a colour reagent. S. Hünig, J. Utermann and G. Erlemann (Chem. Inst. Univ. Marburg, Germany). *Chem. Ber.*, 1955, **88** (5), 708–712.—*p*-Aminodimethylaniline hydrochloride (**I**) gives a sensitive colour reaction with unsaturated carbonyl compounds. A large number of polyenals and polyenones (*cf.* Hünig and Utermann, *Anal. Abstr.*, 1955, **2**, 2747) are shown to give colours ranging from yellow to blue, according to the number of conjugated double bonds. Spectra are given for several of these substances. The reaction involves the use of a double salt of **I** with $SnCl_2$ [prepared by mixing hot alcoholic soln. of **I** (1 mole) and $SnCl_2$ (1 mole)]; the double salt, $C_8H_{12}N_2.H_2SnCl_4$, separates out when the soln. is cooled. As an example, equal volumes of solution A [9-furylnonatetraenal (10·01 mg) in dimethylformamide (2 ml) to which is added dibenzyl sulphide (0·2 g), the soln. being made up to 50 ml with absolute methanol] and solution B [the double salt (39·87 mg) of **I** with $SnCl_2$ dissolved in methanol (100 ml)] are mixed and the temporary increase of the extinction is followed at the absorption maximum. During the period when the extinction is constant, the spectrum between 350 and 800 mμ is measured. The coloured soln. is compared with a soln. containing soln. B

and *C* [dimethylformamide (0·2 ml) and dibenzyl sulphide (0·2 g) in methanol (50 ml)] in equal proportions.   C. A. SLATER

1400. The chromatographic semi-micro analysis of gases. XII. The separation and analysis of gaseous hydrocarbons. J. Janák, M. Rusek and A. Lazarev (Inst. Petrol. Res., Brno, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1955, **20**(5), 1199–1205.— The separation of mixtures of homologous cyclo-paraffins (*e.g.*, cyclopropane and methylcyclopropane, and cyclopropane and cyclobutane) on silica gel and charcoal at 20° C and 80° C is described. The sorption on silica gel increases with the increasing energy content, *i.e.*, strain, for hydrocarbon molecules having the same number of carbon atoms and does not depend on the boiling point. The order of elution of mixtures of gases containing either 2 or 3 carbon atoms is, *e.g.*, ethane, ethylene, acetylene and propane, cyclopropane, propylene, propyne. The quantitative analysis of a mixture of air, CO, ethane, ethylene, propylene and cyclobutane with an error of 0·4 per cent. and of anaesthetic mixtures of air, He, O, N_2O, ethylene and cyclopropane with an error of 1 per cent. is possible.
        P. S. STROSS

1401. Analytical applications of the photochemical action of light. II. Determination of oxalic acid by photo-oxidation in presence of ferric salts. G. Gopala Rao and G. Aravamudan (Andhra Univ., Waltair, India). *Anal. Chim. Acta*, 1955, **13** (5), 415–418.—From 0·2 to 1 mg-equiv. of oxalic acid can be determined accurately by the method described. A mixture of $\simeq 0.05\,N$ oxalic acid (10 ml), 0·1 *N* ferric alum (10 ml) and 4 *N* H_2SO_4 (10 ml) diluted to $\simeq 50$ ml is exposed to sunlight in a quartz beaker for 15 to 30 min. After the reaction is complete (disappearance of the yellow colour), the $Fe^{\cdot\cdot}$ formed are determined by titration with standard $NaVO_3$ soln., with either diphenyl-benzidine or diphenylaminesulphonate as internal indicator in the presence of H_3PO_4. The oxalic acid equiv. of $Fe^{\cdot\cdot}$ is then calculated. An excess of ferric alum (Fe to $C_2O_4'' \nless 4$) must always be present. Formic acid does not interfere.
        W. J. BAKER

1402. The action of sulphuric acid in colour reactions of organic compounds. Detection of mono-chloroacetic acid and other compounds splitting off formaldehyde. F. Feigl and R. Moscovici (Minist. Agric., Rio de Janeiro, Brazil). *Analyst*, 1955, **80**, 803–806.—The role of H_2SO_4 in tests that can be conducted only in its presence is discussed and particularly its action in a new test for chloro-acetic acid, in which it acts as water donor, dehydrating agent and oxidising agent. In this micro-test the chloroacetic acid is maintained at 105° C for 30 min. and is then treated with a few drops of conc. H_2SO_4 and a few grains of solid chromotropic acid, and the mixture is heated to 170° C. The glycollic acid first formed ultimately liberates formaldehyde, which yields a violet colour with chromotropic acid. The heating may also be done in the gas-absorption apparatus commonly used for spot tests, and the formaldehyde is detected in the gaseous phase. Application of the test to certain other compounds is indicated. The similar test for 2 : 4-dichlorophenoxyacetic acid described by Freed (*Science*, 1948, **107**, 98) is apparently based on the same reaction, *i.e.*, hydrolysis of phenoxy-acetic acid to glycollic acid by the H_2SO_4 and subsequent liberation of formaldehyde.
        A. O. JONES

1403. Determination of acetic anhydride by means of aniline. G. V. Zavarov (M. I. Kalinin Chernore-chenskiĭ Chemical Works). *Zavod. Lab.*, 1955, **21** (7), 791–795.—The aniline method (Menshutkin and Vasil'ev, *J. Soc. Phys.-Chim. Russe*, 1889, **21**, 188) for determining acetic anhydride in admixture with acetic acid is based on titrations with NaOH solution before and after the addition of aniline. An improved method based on acetylation in aq. medium and hydrolysis of the anhydride in the presence of pyridine is proposed. *Procedure*—For the aniline method, 100 ml of 3 per cent. aniline in water and 2 g of the sample are shaken together and at once titrated with 0·5 *N* NaOH to phenol-phthalein. For the pyridine method, 100 ml of water, 10 drops of pyridine and 1 g of the sample are mixed together and, after dissolution of the sample, are titrated with 0·5 *N* NaOH. The methods have been checked by boiling 20 g of the anhydride with a 6 to 8 per cent. excess of water and determining the crystallisation point of the acetic acid formed.
        G. S. SMITH

1404. Microscopic identification of microgram quantities of L-arabinose and L-fucose. Direct synthesis of crystalline 2 : 4-dinitrophenylhydrazone and 1 : 1-diphenylhydrazone derivatives by solvent diffusion technique. G. E. Secor and L. M. White (Agric. Res. Service, U.S. Dept. Agric., Albany, Calif., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1998–1999.—The method is an extension of that by White *et al.* (*Anal. Abstr.*, 1955, **2**, 3427) in which microgram quantities of some pure and chromatographically separated pentoses and hexoses were identified by direct synthesis and microscopic examination of their 2 : 4-dinitrophenylhydrazones. The modified method enables L-arabinose to be identified. A similar test is described for determining L-arabinose and L-fucose as their crystalline 1 : 1-diphenyl-hydrazones. As little as 1 to 10 *μg* of the pure or 5 to 15 *μg* of the chromatographically separated pentose is sufficient for the test.   G. P. COOK

1405. A new method for determining ketohexoses in the presence of aldohexoses. M. A. Jermyn (Wool Textile Res. Lab., C.S.I.R.O., Parkville, Victoria, Australia). *Nature*, 1956, **177**, 38–39.— The anthrone method (*cf.* Dreywood, *Brit. Abstr. C*, 1946, 280; Black, *Brit. Abstr. C*, 1952, 207; and Jermyn, *Aust. J. Biol. Sci.*, 1955, **8**, 543) may be used for the quant. determination of ketohexoses and their derivatives in the absence of methylpentoses, an excess of pentoses (a 10-fold excess of xylose over fructose gives a 40 per cent. error) and a large excess of aldohexoses (a 50-fold excess of glucose over fructose gives a 15 per cent. error). Colour develops in a mixture of anthrone reagent with ketose, but not with aldose soln., after the soln. has been left to stand in the cold and, although the heat of mixing is dissipated after 15 min., the extinction continues to increase for periods up to 24 hr. The extinction at 625 m*μ* is proportional to ketose concn. in the range 0·001 to 0·003 *M*. The method is less sensitive than the estimation of total carbohydrate by heating but, in the investigation of the elution of sugars from charcoal columns, results were satisfactory. The application of the method to the incompletely resolved peaks of sucrose and lactose eluted from a charcoal column is illustrated.   O. M. WHITTON

1406. Rapid estimation of dialdehyde content of periodate oxystarch through quantitative alkali consumption. B. T. Hofreiter, B. H. Alexander

and I. A. Wolff (U.S. Dept. Agric., Peoria, Ill., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1930–1931.—The method is based on the quant. consumption of alkali by the dialdehyde content of periodate-oxidised starches and has a simple titrimetric end-point with phenolphthalein indicator. Close agreement with other methods was obtained. The average standard deviation for completely oxidised samples was ±1·88 per cent.　　　G. P. COOK

1407. **Polarographic determination of ethyl nitrate and ethyl nitrite in aqueous solutions.** É. A. Blyumberg and V. L. Pikaeva (Inst. Chem. Phys. Acad. Sci., Moscow). *Zh. Anal. Khim.*, 1955, **10** (5), 310–314.—In 0·1 N LiCl the $E_{\frac{1}{2}}$ of the waves of ethyl nitrate and ethyl nitrite are $-0·70$ and $-0·96$ V *vs.* the S.C.E. The potentials do not vary with pH, but are greatly affected by the presence of ethanol or ether. A polarographic method of determining solubilities of substances is suggested and applied to the determination of the solubility of ethyl nitrate. The diffusion current is plotted against the concn. The curve is first a sloping straight line corresponding to linear relationship between current and concn., which flattens off into a horizontal line corresponding to saturation of the solution. A straight line through the initial part of the curve cuts the horizontal portion produced backwards at a point corresponding to the solubility of the material. The solubility of ethyl nitrate in water at 20° C is thus found to be $\simeq 1·3$ g per 100 g.　　　G. S. SMITH

1408. **Hydrazine method for determining dimethylamine in mixtures containing ammonia and methylamines.** N. F. Alekseev and M. P. Dvinyanina. *Zavod. Lab.*, 1955, **21** (10), 1166–1168.—The sample for analysis should contain $\not>$ 25 g per litre of total amines and ammonia which may be in the form of the free bases or an aq. solution of the salts. The sample (10 to 25 ml) is neutralised to methyl red with 3 N HCl, and 10 ml of 40 per cent. NaNO₂ solution and 6 ml of glacial acetic acid are added. After 10 min., the HNO₂ is destroyed by running into the solution at 0° C a solution of 150 g of sulphamic acid per litre until separation of gas bubbles ceases, and then 3 or 4 ml in excess. The solution is then treated with 10 ml of conc. HCl and 15 g of granulated Zn and is stirred for 20 to 25 min. The liquid is poured into a titration vessel, the Zn being washed with small portions of water, 70 ml of conc. HCl are added, the solution is cooled to room temp., and then titrated with 0·1 or 0·5 N KIO₃.　　　G. S. SMITH

1409. **Characterisation of some hydroxy-ethylated compounds.** G. Carrière. *Fette u. Seifn*, 1955, **57** (8), 563–564.—For an ethoxylated alkylphenol having the formula $H(CH_2)_aC_6H_4\cdot(OC_2H_4)_b\cdot OH$, the values of a and b are found by determining the molecular weight (cryoscopically in benzene) and the molecular refraction (Lorentz - Lorenz formula), known atomic refraction values being used. Good results are obtained when the method is applied to commercial surface-active agents and detergents of known constitution.　　　E. HAYES

1410. **Polarographic determination of acrylonitrile in presence of potassium persulphate.** S. F. Strause and E. Dyer (Univ. Delaware, Newark, Del., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1906–1908.—The method described depends on the fact that under the polarographic conditions described the i_d for vinyl cyanide and K˙ are additive; 0·2 M tetramethyl-

ammonium iodide is used as supporting electrolyte and 0·015 M quinol is added to prevent the oxidation of the iodide by S_2O_8''. A preliminary knowledge of the relative concn. of both components is required so that the final diluted sample may give a diffusion current which falls within the range covered by the calibration studies.

D. G. HIGGS

1411. **Determination of [mixtures of] $\beta\beta'$-oxydipropionitrile[di-(2-cyanoethyl) ether] and ethylene cyanohydrin with acrylonitrile by infra-red absorption.** E. F. Dupre, A. C. Armstrong, E. Klein and R. T. O'Connor (Sthn. Reg. Res. Lab., New Orleans, La., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1878–1879.—An infra-red study of a mixture of the specially purified compounds di-(2-cyanoethyl) ether (**I**), 2-cyanoethanol (**II**) and vinyl cyanide (**III**) showed that each absorbed strongly in the 8 to 11-μ region at wavelengths affected only slightly by the other two components. A series of three simultaneous equations has been calculated so that for the absorption values of each component at the three chosen wavelengths the relative composition can be determined. The absorption is proportional to concn. over the range 1 to 11 μg per litre and accuracy is better than ±2 per cent. of the content.　　　D. G. HIGGS

1412. **The radiometric determination of compounds containing radio-sulphur. Quantitative analysis of ³⁵S-labelled thiourea.** S. H. Götte and G. Theis (Max-Planck Inst. Chem., Mainz, Germany). *Angew. Chem.*, 1955, **67** (21), 637–642.—A full description is given of the Hevesy and Paneth radiometric methods of quantitative analysis in which the determination is effected by measurement of the radioactivity of marked elements. The use of these methods for determining the thiourea absorbed in oranges preserved by treatment with aq. thiourea solution is described. The fruit is soaked in 2 per cent. aq. [³⁵S]thiourea solution and radiometric estimations are made of the [³⁵S]thiourea content of the peel and pulp, by ashing the material with fuming HNO₃, converting the SO₄'' into BaSO₄ and measuring its radioactivity. To determine whether the thiourea absorbed by peel and pulp is chemically combined or remains free, samples of peel and pulp are extracted with alcohol till the alcohol extracts are no longer radioactive, and the extracts are analysed for S by the indicator-dilution method. Radioactive thiourea (1 g) is dissolved in the extracts, fractions of the solutions are floated on toluene and evaporated in aluminium dishes to form films, and the activity of the films is determined. The amount of thiourea present is obtained by comparison of this activity with the activity of a similar film of [³⁵S]thiourea. The results obtained are lower than those obtained by the sulphate ash method, but the difference is not sufficient to account for any chemical combination of thiourea with either peel or pulp. The analyses show that 5 to 11 mg of thiourea are absorbed per 100 g of peel and 0·1 to 0·3 g per 100 g of pulp.　　　H. L. WHITEHEAD

1413. **Separation and identification of phenols by paper chromatography.** J. Green and S. Marcinkiewicz (Vitamins Ltd., Tadworth, Surrey, England). *Nature*, 1955, **176**, 1172–1173.—A technique for separation and identification of closely related monohydric phenols is described. It consists of a first-dimensional separation by adsorption chromatography on paper impregnated with zinc carbonate, with benzene as the developing solvent,

followed by second-dimensional reversed-phase partition chromatography on the same paper impregnated with a 5 per cent. soln. of ethyl oleate in light petroleum. Values for R (measured from the leading edge of the spot) in the first dimension and R_F values in the second dimension are given and discussed for 16 phenols.   O. M. WHITTON

1414. X-ray diffraction patterns of phenols. L. J. E. Hofer and W. C. Peebles (Bur. of Mines, Bruceton, Pa., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1852–1856.—X-ray diffraction analysis is proposed for the positive identification of crystalline phenols which, if of reasonably high m.p., need not be converted into their phenylcarbamates. *Procedure*—The finely ground specimen is partly extruded, without binder material, immediately before use from a stainless-steel tube (internal diameter, 0·7 mm). The specimen was exposed in a Debye - Scherrer camera (diameter, 114·6 mm) for 6 hr. to obtain the long spacings up to 19 A in the small-angle region and then over-exposed in another camera (diameter, 57·3 mm) for 2 hr. to obtain the shorter spacings in the large-angle region. K_α radiation ($\lambda = 1\cdot937$ A) was obtained from a tube equipped with an iron anode, beryllium windows and filters of MnO_2. The intensities were estimated with a calibrated strip prepared by exposure of similar film strip to FeK_α radiation, a decimal stopwatch being used, for times between 0·025 and 3·200 min. The strip was developed under identical conditions and for the same time as for the film containing the patterns. The patterns of isomers and closely related compounds are distinctly different. Powder diffraction data for 51 compounds are listed.   D. G. HIGGS

1415. Quantitative infra-red analysis of alkylphenol mixtures. F. V. Fair and R. J. Friedrich (Pittsburgh Consolidation Coal Co., Pa., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1886–1888.—A method is described for the quantitative determination of the distribution of phenols, the three cresols, the six xylenols and several trimethylphenols. Separation is effected by treatment with NaOH and, after liberation of the tar acids, the mixture is dried in an azeotropic drying apparatus. Fractions are obtained by distillation at 50 mm (Hg) from a column containing ≮25 theoretical plates, over the temperature ranges of original b.p. to 113° C, 113° to 121° C, 121° to 127° C, 127° to 134° C and 134° to 144° C. Infra-red data are obtained by the use of approx. 2 per cent. soln. of phenols in CS_2 in 0·1-mm cells and optics of NaCl. Calibration of the instrument is originally made against a range of 1·5 to 2·5 per cent. soln. in CS_2 of specially purified isomers. The method can be completed in 24 manhours and the overall absolute accuracy is ±1 per cent.   D. G. HIGGS

1416. Determination of molecular weight of the *m*-polyphenyls by measuring their absorbance. L. Silverman and W. Houk (N. Amer. Aviation Inc., Nuclear Eng. and Manufacturing, Downey, Calif., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1956–1957.—At the wavelength of max. absorbance, usually between 250 and 260 mμ, the absorbance of the *m*-polyphenyls decreases with increasing molecular wt. Since the values are directly related, an unknown sample can be determined by measurement of its absorbance, the mol. wt. being read from a standard curve. The molecular wt. of polyphenyls containing up to 12 phenyl groups can be determined by this method.   G. P. COOK

1417. Identification of amines. I. N-(Arylaminomethyl)phthalimides. M. B. Winstead and H. W. Heine (Bucknell Univ., Lewisburg, Pa., U.S.A.). *J. Amer. Chem. Soc.*, 1955, **77**, 1913.—The reaction of phthalimide and formaldehyde with primary aromatic amines to produce N-(arylaminomethyl)-phthalimides is shown to be general and is particularly useful for the identification of aromatic amines. These derivatives are easy to prepare and purify and all have melting points between 110° and 235° C. The preparation is carried out by suspending phthalimide (3 g) in boiling 80 per cent. ethanol, adding 37 per cent. formaldehyde (2 ml) and refluxing until all the imide has dissolved. A soln. of the aromatic amine (0·023 mole) in 80 per cent. ethanol (10 ml) is added. The mixture is refluxed for 30 min. (or 1 hr. if the amine possesses a *meta*-directing group). On being cooled the derivative crystallises. Melting points are given for the N-(arylaminomethyl)phthalimides derived from 30 aromatic amines.   C. A. SLATER

1418. The determination of *cyclo*pentadiene and maleic anhydride. P. Unger (Brit. Scientific Instrum. Res. Ass., Chislehurst, Kent, England). *Analyst*, 1955, **80**, 820–824.—*cyclo*Pentadiene and maleic anhydride interact to form *cis*-3:6-*endo*-methylenetetrahydrophthalic anhydride (carbic anhydride). This is easily hydrolysed to carbic acid, which absorbs Br quant. at the double bond. In the method described the sample is treated with maleic anhydride reagent (3 per cent. w/v in pure benzene) at 35° C for 10 min. An aliquot portion is diluted with amyl acetate and the carbic acid is extracted with aq. KOH soln. The alkaline extract is acidified and titrated with 0·1 N KBrO₃ - KBr soln. until a slight excess of Br persists. This excess is determined by the addition of KI and titration of the liberated I with $Na_2S_2O_3$ soln. Di*cyclo*-pentadiene interferes only very slightly. Maleic anhydride is determined by reaction with a *cyclo*-pentadiene reagent and determination of the residual *cyclo*pentadiene by the method described. Maleic acid and saturated acids and anhydrides do not interfere. The accuracy of the method is within ±0·3 per cent.   A. O. JONES

1419. Spectrophotometric determination of furfuraldehyde and hydroxymethylfurfuraldehyde in carbohydrate hydrolysates. E. Lindemann (Bundesforschungsanstalt Getreideverarbeitung Detmold, Germany). *Stärke*, 1955, **7**, 280–284.—Wood and starch hydrolysates contain furfuraldehyde (**I**) and 5-hydroxymethylfurfuraldehyde (**II**), respectively, and a method for their determination is described. **I** is removed by steam-distillation and determined separately. Measurement of the extinction is made at 275 mμ for **I** and at 284 mμ for **II**. In each case the extinction measured with pure water at 245 mμ is subtracted from the reading, and the actual amount of **I** present is obtained by referring the result to calibration tables. Concentrations of **I** and **II** of less than 1 mg per litre may be determined.   E. DUX

1420. Determination of α-, β- and γ-picolines, 2:6-lutidine and 2-ethylpyridine in the β-picoline fraction of pyridine bases. E. Knobloch (Výzkumný ústav pro farm. a biochem., Prague, Czechoslovakia). *Chem. Listy*, 1955, **49** (2), 268–271.—Infra-red spectroscopy permits the determination of α-, β- and γ-picolines, 2:6-lutidine and 2-ethylpyridine, simultaneously present in the β-picoline fraction of pyridine bases, with an accuracy of ±2 per cent.   G. GLASER

1421. **Type carbon atom analysis of heavy hydro-carbon products.** S. Miron (Amer. Oil Co., Texas City, Tex., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1947–1955.—A method is described for the determination of the aromatic, naphthenic and alkyl carbon atom content of hydrocarbons of molecular wt. > 150. Aromatic and olefinic hydrocarbons are differentiated by selective hydrogenation over a nickel catalyst, a low temp. ($\simeq 130°$ C) being adopted for the hydrogenation of the olefinic double-bonds; temp. > 180° C are needed for aromatic double-bond hydrogenation. The ring content is computed from the molecular formula after complete hydrogenation, and the average ring size is determined by using the molecular wt. - density correlations of Kurtz and Lipkin. In some instances the degree of ring condensation is calculated from measurable quantities, and for all others an assumption of 50 per cent. condensation is made. Possible relative errors of the method were calculated and varied from −22·5 per cent. to +50·0 per cent., but were generally less than those of an alternative procedure. The method was applied to seven hydrocarbons.　　　　G. P. COOK

1422. **Laboratory methods for evaluation of evaporation losses of petroleum products.** J. Holowchak and E. L. Baldeschwieler (Esso Res. and Eng. Co., Linden, N.J., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1941–1947.—Two methods are described for the measurement of evaporation loss. The first is a modified Chenicek - Whitman vapour-pressure method (*Oil Gas J.*, 1930, **29**, 78), and in the second procedure a density - evaporation curve is established to determine the effect of the evaporation loss on the density of the sample. With the vapour-pressure method, evaporation losses as low as 0·04 per cent. can be accurately determined, and with the density method losses as low as 0·01 per cent. can be detected. Close agreement is obtained between the two methods.　　　　G. P. COOK

1423. **Determination of trace metals in [petroleum] oils.** J. T. Horeczy, B. N. Hill, A. E. Walters, H. G. Schutze and W. H. Bonner (Humble Oil & Refining Co., Baytown, Tex., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1899–1903.—Wet- and dry-ashing procedures are discussed in relation to their validity for determining p.p.m. of metals in different petroleum distillates. The rapid and accurate wet-ash (sulphation) method described depends on the quant. recovery of the metals from their volatile porphyrin complexes in the oil, and is a modification of a previous procedure (Milner *et al.*, *Brit. Abstr. C*, 1953, 119). The sample ($\simeq 100$ g) is heated rapidly with conc. H_2SO_4 (1 ml per g of sample) in a beaker, first at 800° F (hot-plate) to a dry coke, and finally at $\simeq 1000°$ F (muffle-furnace) in air or oxygen until an inorganic ash remains. The residue is dissolved in 20 ml of HCl (1 + 1) and the vol. is adjusted to 100 ml with water. Aliquots of this soln. are then taken for the determination of Ni by dimethyl-glyoxime, Fe by thiocyanate, V by tungstophosphate, and Cu by polarography. The reagent blanks are also determined; if the blank for Cu is very high, low concn. of Cu in the sample cannot be determined. Results obtained with synthetic blends containing from 0·2 to 20 p.p.m. of each metal as the tetraphenylporphyrin complex are reported and are shown to be more accurate than those of the dry-ashing procedure (*Brit. Abstr. C*, 1953, 120), in which recovery of the metals is not quant. The prep. of tetraphenylporphyrin and its Ni, Cu, V and Fe deriv. are described.　　　W. J. BAKER

1424. **Quantitative spectrographic determination of vanadium in petroleum products by logarithmic sector method.** J. A. Kanehann (Socony Mobil Lab., Brooklyn, N.Y., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1873–1874.—A rapid method is described for the spectrographic determination of V in petroleum residues to which Ti is added as internal standard; the residue is diluted with a buffer of graphite and SiO_2, and a logarithmic disc sector is employed, thus dispensing with the need for plate calibration. The determination of V can be completed in 1 hr. by one operator. Results in general compared very favourably with those by the normal densitometer method and the technique has the advantage of speed; expensive equipment is not needed.
　　　　　　　　　　　　　　　　D. G. HIGGS

1425. **Spectrographic determination of nickel and vanadium in petroleum products by catalytic ashing.** J. E. McEvoy, T. H. Milliken and A. L. Juliard (Houdry Process Corp., Marcus Hook, Pa., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1869–1872.—Traces of Ni and V in different types of oil can be rapidly determined with reasonable accuracy by ashing the oil with 7 to 50 per cent. of SiO_2 - Al_2O_3, which catalytically decomposes the sample, and analysing the ignited product spectrographically. The results compare very favourably with those obtained by wet ashing of the oils followed by photometric determination of their metal content. Three types of treatment are discussed: (*i*) blend procedure, (*ii*) drop procedure and (*iii*) acid decomposition of the oil. *Drop procedure*—This appears to be the cleanest mode of decomposition of the oil and consists in adding the oil, dropwise, to the heated SiO_2 - Al_2O_3 catalytic mixture (2 g), contained in a porcelain crucible at $\simeq 250°$ C, at such a rate that it is completely absorbed, cracked and vaporised within $\simeq 0·5$ sec. (*i.e.*, $\simeq 2$ drops per min.); the temperature is adjusted to effect the balance described and the catalyst is occasionally stirred to assist uniform cracking of the oil. The catalyst and the absorbed metal ions are ignited at 600° C for 2 hr. The mixture is finally ground, blended with a mixture of graphite and Cr_2O_3, pelleted and arced under closely controlled spectrographic conditions (exposure and excitation conditions given). Reproducibility is generally better than ±5 per cent. and experiments on many types of oil indicate that the accuracy of the catalytic method, compared with the spectrophotometric determination after wet decomposition, is generally within ±15 per cent.
　　　　　　　　　　　　　　　　D. G. HIGGS

1426. **The identification of fuel oils polluting coastal waters.** J. K. Johannesson (City Council Lab., Wellington C.1, New Zealand). *Analyst*, 1955, **80**, 840–841.—The usual methods of oil identification (*e.g.*, viscosity and flash point) are of no value with oils that have become emulsified with water or have been floating as thin films. The method described depends on the determination of the Ni and V contents of the oils. The amounts of these elements occurring in the ash of the oils vary considerably; figures as high as 22·15 per cent. of V_2O_5 and 5·89 per cent. of NiO occur in some quoted results. The sample (3 to 5 g according to the amount of emulsified water present, determined by a Dean and Stark distillation) is ashed in a platinum basin, ethanol being added to promote removal of water and the burner flame being initially directed on the surface of the liquid. The metals may be detected by the methods of Wrightson (*Brit. Abstr. C*, 1950, 227) or any other suitable

methods. Vanadium and Ni occur in the oils as co-ordinated complexes with porphyrins.

A. O. JONES

1427. A test for pitch and bitumen. A. D. Baynes-Cope (Government Lab., London). *Analyst*, 1955, **80**, 839–840.—In the test described, paper chromatography is used to separate from pitch and bitumen substances that have a characteristic fluorescence in u.v. light. A speck of the sample is pressed on to a Whatman No. 4 paper strip 1 cm from the end and the paper is eluted with toluene until the front has moved 4 to 5 cm past the origin. The dried paper is again eluted with dry methanol until the front is ≃ 8 cm beyond the origin. When dry, the paper is examined in u.v. light. Bitumen shows an orange - brown streak ending at the toluene front. Coal-tar pitch shows a brilliant blue streak, often bifurcated, extending from the area behind the toluene front almost up to the methanol front. Mineral grease or oil shows a dull-blue streak entirely behind the toluene front. Creosote and creosote residues behave as pitch. Application of the test to the estimation of small amounts of bitumen in coal-tar pitch is described.

A. O. JONES

1428. The differentiation of long-chain cation-active compounds from ampholytes and amine salts. R. Neu. *Fette u. Seifen*, 1955, **57** (8), 568–570.—When 1 ml of a 1 per cent. aq. soln. of a long-chain quaternary ammonium compound is treated with 1 ml of a 0·1 per cent. soln. of 3:5:7:3′:4′-penta-hydroxyflavone in methanol and then with 0·5 ml of a freshly prepared 0·5 per cent. methanolic soln. of tetraphenyl diboroxide, a red or orange ppt. is produced; the ppt. is stable to aq. NH₃ soln. A similar ppt. is given by long-chain amine salts and ampholyte-active compounds, but with these the ppt. is dissolved when 2 ml of 2 N aq. NH₃ soln. are added. The reaction can be used to distinguish the two classes of compounds, and is useful in the examination of commercial surface-active agents. Short-chain quaternary ammonium compounds give no ppt.

E. HAYES

1429. Estimation of sulphite and other reducing substances in photographic gelatin. H. W. Wood (Ilford Ltd., Ilford, Essex). *J. Photogr. Sci.*, 1955, **3** (5), 144–149.—The method of estimating sulphite based on steam-distillation is complicated by the presence of thiosulphate, nitrite, reductone, etc., which affect the iodine consumption in the titration. The residual reducing substances may be determined after removal of free sulphite with formaldehyde. Gelatin (10 g) is soaked in 150 ml of water for 1 hr. and dispersed by warming at 40° to 45° C. Formaldehyde (40 per cent.) (2 ml) is added, the mixture is set aside for 5 min., then poured into 150 ml of water containing 1 ml of N KI, and adjusted to pH 3·0 with 5 N H₂SO₄. The solution is titrated potentiometrically (bright platinum and calomel electrodes) with 0·001 N I until the observed potential has risen to 340 mV. The estimation of total reducing substances, including sulphite, is performed by a method of successive approximations. Sifted gelatin (10 g) is warmed to 45° C in a closed flask with 2 ml of N NaOH and 150 ml of water, then the solution is blown by a stream of nitrogen into 150 ml of water containing x ml of 0·02 N iodine, 5 ml of 5 N H₂SO₄ and 5 ml of N KI. Starch solution (1 per cent.) (5 ml) is added and the mixture is back-titrated with 0·02 N Na₂S₂O₃. If the uptake of iodine is y ($< x$)

ml, the next run is carried out with y instead of x ml of iodine. The procedure is continued until the excess of iodine is $< 0·1$ ml, which gives the final result.

S.C.I. ABSTR.

1430. Determination of cellulose in *Stipa tenacissima* L. (esparto). A. Torner Ochoa, J. Marcos de Lanuza and A. Rodríguez Socorro (Servicio del Esparto, Madrid). *Rev. Cienc. Apl.*, 1955, **9** (45), 327–333.—Statistical analysis was applied to a large number of determinations of cellulose in esparto, with both the method of chlorination (Sieber and Walter, *Papierfabrikant*, 1913, **11**, 1179) and the Belluchi method of oxidation with a mixture of HNO₃ and acetic acid [Pratolongo, "*Analisi Chimico-agrarie*," 1952 (Milan)]. It is seen from the results that waxes, fats, etc., must first be removed from the crude esparto by extraction with ethanol - benzene (1 : 2); chlorination gives values higher than theoretical because of incomplete elimination of the hemicelluloses; the characteristics of the cellulose obtained make it advisable to use the chlorination method for precise determinations, completing with an estimation of the hemicelluloses or copper index, etc.; for rapid determinations the oxidation method with HNO₃ - acetic acid is accurate enough.

D. LEIGHTON

1431. The analysis of chemical products used in perfumery. W. D. Fordham (A. Boake Roberts & Co. Ltd., Stratford, London). *Industr. Parfum.*, 1955, **10**, 62–64.—The use of infra-red spectroscopy in the detection and quant. evaluation of trace impurities in pure chemicals, with citronellol in geraniol as an example, is discussed. In this instance the extinction at 1059 cm⁻¹ is a linear function of the percentage of citronellol present (up to 20 per cent.). For trace contamination, greater accuracy is attained by prior fractional distillation of the mixture. In another method the acetoacetic ester of the alcohol is prepared; this is converted into the *p*-nitrophenylhydrazone or the more stable 4-phenylsemicarbazone. The m.p. of the product is an indication of the purity of the alcohol.

H. B. HEATH

1432. The absorptiometric determination of poly-(ethylene glycol mono-oleate). E. G. Brown and T. J. Hayes (British Enka Ltd., Aintree, Liverpool). *Analyst*, 1955, **80**, 755–767.—A method is described for the determination of poly(ethylene glycol mono-oleate) (I) in aq. soln. The sample is treated with ammonium cobaltothiocyanate soln. (prep. described) in a specified manner and the mixture is extracted with chloroform. The chloroform extract is cleared by centrifuging and its extinction is measured at 318·5 and 620 mμ against chloroform as reference liquid. The calibration graph is prepared with weighed portions of **I** dissolved in water and submitted to the procedure described, which is applicable at concn. up to 1 g per litre. The extension of the method to other poly(ethylene glycols) and their derivatives and to some quaternary ammonium compounds was investigated qualitatively.

A. O. JONES

1433. Examination of an interpolymer of poly-caproamide, poly(hexamethylenediamine adipamide) and poly(*p*-diaminodicyclohexylmethane adipamide) (Nylon 6, Nylon 66 and Nylon PACM 6). M. Clasper, J. Haslam and E. F. Mooney (I.C.I. Ltd., Plastics Div., Welwyn Garden City, Herts., England). *Analyst*, 1955, **80**, 812–819.—A detailed description

is given of the methods used for the examination of the above-mentioned interpolymer. Hydrolysis with HCl, followed by extraction with ether, yielded adipic acid. The aq. liquid remaining, when evaporated to dryness, contained 26·1 per cent. of Cl, which is different from the Cl content of hexamethylenediamine dihydrochloride (I) or ε-aminocaproic acid hydrochloride (II) and the interpolymer had an unfamiliar i.r. spectrum. The mixed-base hydrochloride was dissolved in water and titrated with 0·1 N NaOH to determine II, and the identity of the titratable hydrochloride with II was established by passing the mixed-base hydrochloride through an Amberlite IRA-400 resin column previously treated with NaOH. The solid residue from the HCl eluate of the column had an i.r. spectrum identical with that of II. The original eluate from the column containing the bases of I and p-diaminodicyclohexylmethane dihydrochloride (III) was subjected to a procedure whereby III was separated and identified by its i.r. spectrum. Further proof that the mixed-base hydrochloride did in fact behave as a mixture of I, II and III was obtained chromatographically.

A. O. JONES

1434. Decomposition and determination of pentaerythritol in alkyd resins. J. Mleziva. *Fette u. Seifen*, 1955, **57** (9), 691–693.—In the determination of pentaerythritol in alkyd resins by aminolysis with 2-phenylethylamine, washing with chloroform and weighing, Kappelmeier (*Anal. Abstr.*, 1955, **2**, 2789) obtained low results, which he attributed to the solubility of pentaerythritol in chloroform and in the small amount of glycerol present. Other methods also give low results, lower than the calculated values. The low results are real and not apparent, being due to the thermal decomposition of some of the pentaerythritol during the formation of the resin. E. HAYES

1435. Determination of free sulphur in vulcanisates. I. T. Taranenko and I. A. Zakharova (Central Sci. Res. Lab. Asbotechnical Articles). *Zavod. Lab.*, 1955, **21** (10), 1163–1166.—The determination of free S in rubber from the sulphur content of the acetone extract is unsatisfactory, since acetone is a very poor solvent for S and also extracts certain sulphur-containing compounds. Moreover the method takes a long time. The sulphite method of Bolotnikov and Gurova (*Zh. Rezin. Prom.*, *SSSR*, 1933, 6) is quicker and more accurate, but some sulphur compounds react. The use of diethylamine is now recommended. It reacts completely and rapidly with free S even when the solvent is greatly diluted with water. Thus a solution of 25 ml of 100 per cent. diethylamine and 75 ml of water dissolves S in 40 to 45 min. at the b.p. *Procedure*— The finely divided sample of rubber (2 g), in a 250-ml conical flask fitted with a condenser, is boiled with a mixture of 25 ml of diethylamine and 75 ml of water for 40 to 45 min. The cooled liquid containing thiodiethylamine [(C₂H₅)₂NSH] is filtered into a 500-ml calibrated flask and the flask and filter are washed with water until the washings give no alkaline reaction to phenolphthalein. The solution is made up to the mark, 50 ml are mixed with 200 to 250 ml of water, 20 ml of 0·05 N KIO₃, 10 ml of 10 per cent. KI solution and 30 ml of 2 N HCl, and the liberated iodine is titrated with 0·05 N Na₂S₂O₃, with starch as indicator. The amount of S is calculated from the reaction—

$(C_2H_5)_2NSH + KIO_3 + 5KI + 7HCl \rightarrow$
$(C_2H_5)_2NCl + 6KCl + 3H_2O + 2HI + S + 2I_2.$
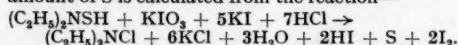
Tests on rubbers first extracted with sulphite showed no free S in the diethylamine extraction. Tests on rubbers first extracted with diethylamine showed free S by the sulphite method, indicating that sulphite reacts with some combined S as well as free S. G. S. SMITH

1436. Determination of natural rubber in GR-S - natural rubber vulcanisates by infra-red spectroscopy. M. Tryon, E. Horowitz and J. Mandel. *J. Res. Nat. Bur. Stand.*, 1955, **55** (4), 219–222.— Samples containing known amounts of natural and GR-S rubber were pyrolysed at 550° C in a combustion cell and the liquid pyrolysate was placed between two sodium chloride windows, with a lead spacer 0·025 mm thick, and the i.r. spectrum was obtained in a recording spectrophotometer with sodium chloride optics. The ratio (Y) of transmittances at wavelengths of 11·02 and 11·25 μ was calculated and log Y was found to be very nearly a linear function of the concn. (X) of natural rubber in the total polymer. A quadratic equation, log Y = 0·730 + 0·00851X − 0·000015 X^2, gives a more accurate relationship. S.C.I. ABSTR.

1437. Note on the filtration of tannin solutions. H. A. Litten (National Leathersellers' College, London). *J. Soc. Leath. Tr. Chem.*, 1955, **39** (9), 300–301.—Apparatus is described to prevent oxidation and evaporation which may occur during filtration of tannin solutions in the determination of insol. matter according to the "Official Methods of Analysis" of the Society of Leather Trades' Chemists. A filter-candle is enclosed in a glass tube in a flask containing the tannin soln. so that the candle is completely covered by the soln. during filtration. B. R. HAZEL

See also Abstracts 1352, 1502, 1522, 1562, 1573, 1578, 1579, 1592.

4.—BIOCHEMISTRY
INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Blood, Bile, Urine, etc.

1438. Spectrophotometric determination of the oxygen saturation of whole blood. M. U. Tsao, S. S. Sethna, C. H. Sloan and L. J. Wyngarden (Univ. Michigan Med. Sch., Ann Arbor, U.S.A.). *J. Biol. Chem.*, 1955, **217** (1), 479–488.—The rapid spectrophotometric method described, in which 0·5 ml of sample is used, is based on the determination of the absorption max. of oxyhaemoglobin and the isosbestic point of oxyhaemoglobin and haemoglobin. The precision is comparable with that of the manometric method and there is a good correlation between the results obtained with both procedures. J. N. ASHLEY

1439. A flame-photometric method for the determination of plasma magnesium after hydroxyquinoline precipitation. S. Davis (Med. Res. Lab., Veterans Admin. Hosp., Indianapolis, Indiana, U.S.A.). *J. Biol. Chem.*, 1955, **216** (2), 643–651.—A new, accurate and sensitive method is described for the determination of Mg in plasma. The Mg is first precipitated as the hydroxyquinoline complex and is then determined by flame photometry. Twenty-four determinations can be carried out in 3 hr. J. N. ASHLEY

1440. A micro-method for determination of serum calcium. H. E. Harrison and H. C. Harrison (City Hosp., Baltimore, Md., U.S.A.). *J. Lab. Clin. Med.*, 1955, **46** (4), 662–664.—Calcium is pptd. as oxalate, dissolved in a measured excess of EDTA soln. and the excess is titrated with standard aq. $CaCl_2$ soln. *Reagents*—(*i*) Mix 0·5 ml of 0·1 N oxalic acid with 10 ml of 0·1 N sodium oxalate. (*ii*) Dissolve 4·5 g of EDTA (disodium salt) in water to 1 litre. Dilute, as required, 2 ml to 10 ml with (*iii*). (*iii*) Dilute 15 ml of ethanolamine to 1 litre with water. (*iv*) Dissolve 0·5 g of Eriochrome black T in ethanolamine to 100 ml. (*v*) Dilute, as required, 0·5 ml of (*iv*) with 2·0 ml of water. (*vi*) Prepare a 0·02 M soln. of $CaCl_2$ from $CaCO_3$. *Procedure*—Place 0·2 ml of serum in a conical 2-ml centrifuge tube. Add 0·2 ml of (*i*) and shake for 30 min. Centrifuge for 5 min. and carefully aspirate off the supernatant liquid. Add 0·50 ml of the diluted (*ii*) and tap the tube gently to dissolve all the ppt. Add 0·05 ml of (*v*) and titrate with (*vi*) from a 0·1-ml microburette, with the tip of the burette under the surface of the liquid. Stir during titration by bubbling air into the solution through a polyethylene tube. Carry out a blank determination and calculate the difference in the amount of (*vi*) required as mg of Ca per 100 ml of sample. W. H. C. SHAW

1441. Determination of cadmium in urine and observations on urinary cadmium and protein excretion in men exposed to cadmium oxide dust. J. C. Smith, J. E. Kench and R. E. Lane (Nuffield Dept. of Occupational Hlth., Univ. Manchester, England). *Biochem. J.*, 1955, **61** (4), 698–701.—An accurate, sensitive and specific dithizone method is described for the determination of cadmium in urine. After all the org. matter has been oxidised, the Cd is converted into the dithizonate and the extinction of the resulting soln. is measured spectrophotometrically at 506 mμ. J. N. ASHLEY

1442. Polarographic determination of uranium in blood. F. Valić and O. A. Weber (Inst. Med. Res., Yugoslav Acad. Sci., Zagreb, Yugoslavia). *Arhiv Kem.*, 1955, **27** (2), 53–57.—A polarographic method has been developed for the determination of trace quantities of U in blood. A liquid - liquid extraction is used after destruction of the blood with HNO_3 and H_2O_2, and the U is polarographed in a supporting electrolyte containing salicylic acid (0·16 per cent.), H_2SO_4 (0·4 per cent.) and thymol (0·009 per cent.). *Procedure*—The blood (5 ml) is heated in a Kjeldahl flask (100 ml) with conc. HNO_3 (15 to 20 ml), added in small amounts after each preceding quantity has evaporated to dryness. When the resulting soln. is almost clear, H_2O_2 (30 per cent.) (10 ml) is added, the whole is gently heated and finally evaporated to dryness. The residue is dissolved in a little water ($\simeq$ 10 ml), then transferred to a micro liquid - liquid extractor. Tetrahydropyran (8 ml) is added and the U is extracted for 2 hr. A resinous product, formed during the extraction, is treated as described above with conc. HNO_3 and H_2O_2; the residue is evaporated to dryness on a water bath and finally ignited at 450° to 500° C. The residue is dissolved by heating with a small quantity of dil. H_2SO_4, on a steam-bath, and again evaporated until only the residue and some H_2SO_4 remain; this vol. of H_2SO_4 is allowed for in the final dilution of the soln. to 500 μl of supporting electrolyte (the composition of which is given above). The volume of soln. is measured in a modified Gorbach membrane micro-pipette.

Oxygen is removed by passing oxygen-free H through the soln. for 10 min. and the polarogram is obtained in the usual manner. The values for wave height were obtained from the vertical distance through the point of $E_{\frac{1}{2}}$ between the extrapolation lines for i_r and i_d; it was found to be linear with C over the range 5 to 400 μg per 100 ml of blood. The standard error for a single determination is ± 25 μg of U per 100 ml of blood. No other polarographic details are quoted. D. G. HIGGS

1443. Determination of urea in blood and urine with diacetyl monoxime. H. L. Rosenthal (Rochester Gen. Hospital, Rochester, N.Y., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1980–1982.—The condensation of urea with acid diacetyl monoxime, followed by oxidation with arsenic acid, was studied to improve reproducibility and linearity of response of the reaction. By performing the reaction in 3·8 N HCl and 0·08 N arsenic acid, a max. colour is obtained which conforms to Beer's law at urea concn. up to 6 μg per ml. These studies formed the basis for the determination of urea in blood and urine; recoveries ranged from 94 to 103 per cent. in blood and 92 to 110 per cent. in urine. G. P. COOK

1444. Enzymic determination of hypoxanthine and xanthine in human plasma and urine. S. Jørgensen and H. E. Poulsen (Dept. Pharmacol., Univ. Copenhagen, Denmark). *Acta Pharmacol. Tox.*, *Kbh.*, 1955, **11** (3), 223–243.—By treatment with xanthine oxidase, hypoxanthine (**I**) or xanthine (**II**) may be oxidised quant. to uric acid (**III**), which can be determined from the increase in extinction at 292·5 mμ. In mixtures of **I** and **II** further treatment with uricase and measurement of the decrease in extinction at 292·5 mμ is necessary to enable the concn. of **I** and **II** to be determined separately. A detailed examination is made of the proposed procedure for carrying out the determinations on protein-free soln. in the presence of neutralised protein precipitants, of the removal of **III** by uricase and of the adaptation of the method for determining **I** and **II** in 0·8-ml amounts of plasma or 0·1 to 0·2 ml of urine. Normal human plasma is found to contain 1 to 3 μg per ml of **I** and **II**, and urine to contain **I** and **II** to the extent of 5 to 10 per cent. of the **III** present. Details are given for preparing and standardising the two enzymes. W. H. C. SHAW

1445. Hypoxanthine and xanthine accumulated in stored human blood: determination of the relative amounts by spectrophotometry. S. Jørgensen (Dept. of Pharmacology, Univ. Copenhagen, Denmark). *Acta Pharmacol. Tox.*, *Kbh.*, 1955, **11** (3), 265–276.—The spectrophotometric method described is based on the known u.v. absorption curves for hypoxanthine (**I**), xanthine (**II**) and for uric acid (**III**) to which **I** and **II** are oxidised in the presence of xanthine oxidase. Fresh or stored heparinised blood is deproteinised and, after dilution of an aliquot to known vol., preformed **III** is removed by incubation with uricase at pH 9·3. The uricase is then destroyed by treatment with excess of aq. NaOH and, after neutralisation to pH 8·2, xanthine oxidase is added and the changes in extinction values at 273 mμ (max. for **II**) and at 292·5 mμ (max. for **III**) are followed spectroscopically. From the final ratio of the extinction values at the two wavelengths, compared with the ratio at zero time for xanthine oxidase addition (determined separately), the amounts of **I** and **II** are calculated. Fresh human whole blood was found

to contain about 10 μmoles per litre of **I** plus **II**, the amount present rising to between 400 and 700 μmoles per litre after storage for 24 hr. at 37° C. In blood from four subjects **I** constituted more than 70 per cent. of the accumulated oxypurines.

W. H. C. SHAW

1446. An improved method for the determination of plasma heparin. H. Engelberg, A. Dudley and L. Freeman (Cedars of Lebanon Hosp., Los Angeles, Calif., U.S.A.). *J. Lab. Clin. Med.*, 1955, **46** (4), 653–656.—In a modification of the method described previously (*Amer. J. Clin. Path.*, 1954, **24**, 599), the initial preparation of the sample is by pptn. of the total serum or plasma proteins with methanol - acetone (1:1), tryptic digestion of the separated proteins and subsequent dialysis and lyophilisation. Anticoagulant activity of the prepared sample is determined as previously (*loc. cit.*). Recovery of endogenous circulating heparin is 75 to 80 per cent., and the deviation from the mean is ± 13 per cent.

W. H. C. SHAW

1447. Determination of 5-hydroxyindol-3-ylacetic acid in urine and its excretion in patients with malignant carcinoids. A. Hanson and F. Serin (Univ. of Lund, Gen. Hosp., Malmö, Sweden). *Lancet*, 1955, **ii** (27), 1359–1361.—Paper chromatography of extracts of urine from patients with carcinoidosis showed that the indole derivatives excreted consisted almost entirely of 5-hydroxyindol-3-ylacetic acid (**I**). As a screening test, 3 ml of urine are mixed with 3 ml of Ehrlich reagent and boiled; a blue colour appears if a pathological amount of **I** is present. The test may be applied to the residue from ether extraction of acidified urine when the concn. of **I** is low or if the urine is highly pigmented. For quant. determination, acidify 2 ml of urine with one or two drops of 10 per cent. HCl and extract twice with 25 ml of ether. Filter, dry the ether with anhyd. Na$_2$SO$_4$ and evaporate to dryness at 50° C on a water bath. Dissolve the residue in 1 ml of 0·1 N HCl and to 0·2 ml of this soln. add 5 ml of Ehrlich reagent. Heat the test together with a blank (0·2 ml of 0·1 N HCl) on a water bath at 45° to 50° C for 2 hr., remove and dilute at once to 10 ml with cold 50 per cent. ethanol; read the colours at 590 mμ. The sensitivity of the method is 5 μg of **I** and for smaller amounts a larger aliquot of the 0·1 N HCl soln. should be taken.

H. F. W. KIRKPATRICK

1448. A rapid chromatographic test for high urinary excretion of 5-hydroxyindol-3-ylacetic acid and 5-hydroxytryptamine. G. Curzon (Nat. Hosp. for Nervous Diseases, Queen Sq., London). *Lancet*, 1955, **ii** (27), 1361–1362.—Urine (50 μl) is applied in 10-μl portions from a micro-pipette and dried by a warm-air current at a point 4 cm from an edge of a rectangular piece of Whatman No. 4 paper. A 5-μl portion of a 1 mg per ml ethanolic soln. of 5-hydroxyindol-3-ylacetic acid (**I**) or of a 0·2 mg per ml aq. soln. of 5-hydroxytryptamine (**II**) may be applied in parallel as well as a normal urine for comparison. The sheet is fastened in cylindrical form with staples and stood in about 100 ml of solvent in a wide-necked jar for 45 min. The chromatogram is dried in a warm-air oven, sprayed with colour reagent (0·2 g of p-dimethylaminobenzaldehyde dissolved in 5 ml of conc. HCl and 95 ml of water added) and heated for 10 to 15 min. at 55° to 60° C. For the detection of **I**, the solvent is 8 g of NaCl dissolved in 100 ml of water and 1 ml of glacial acetic acid. For **II**, the solvent is 8 per

cent. w/v NaCl. Urine containing at least 20 mg of **I** per litre shows a blue - grey spot which travels separately from other indole material and which tends to become stronger on standing. Urine containing at least 2 mg of **II** per litre shows a blue spot separate from other indoles present, which fades on standing.

H. F. W. KIRKPATRICK

1449. The identification of 5-hydroxyindol-3-ylacetic acid in normal urine and a method for its assay. S. Udenfriend, E. Titus and H. Weissbach (Lab. of Chem. Pharmacol, Nat. Inst. of Hlth, U.S. Dept. of Hlth, Educ. and Welfare, Bethesda, Md., U.S.A.). *J. Biol. Chem.*, 1955, **216** (2), 499–505.—A specific method for the identification and determination of 5-hydroxyindol-3-ylacetic acid in urine is described. The urine is treated with 2:4-dinitrophenylhydrazine to remove any keto acids, because these substances interfere with the final colour. Normally, interference is slight, but in some metabolic disorders large amounts of keto acids are excreted and their removal is essential. The dinitrophenylhydrazones are filtered off and the urine is extracted with CHCl$_3$ to remove indolylacetic acid. The aq. phase is then saturated with NaCl, the 5-hydroxyindol-3-ylacetic acid is extracted with ether and returned to 0·5 M PO$_4$''' buffer, pH 7·0. 1-Nitroso-2-naphthol and a nitrous acid reagent (prepared from 2 N H$_2$SO$_4$ and 2·5 per cent. NaNO$_2$) are added and, after warming at 37° C for 5 min., the mixture is extracted with ethyl acetate and the extinction of the coloured aq. layer is measured at 540 mμ. Standard soln. are prepared for comparison and determination of the 5-hydroxyindol-3-ylacetic acid.

J. N. ASHLEY

1450. The effect of suspended solids in thromboplastin preparations upon prothrombin determinations. G. E. Phillips and J. G. Lenahan (Warner-Chilcott Res. Lab., Morris Plains, N.J., U.S.A.). *J. Lab. Clin. Med.*, 1955, **46** (5), 713–719.—It is concluded that there is an optimum concentration of suspended particles, any variation from which prolongs the prothrombin time, particularly in plasma low in prothrombin. An excessive number of particles in thromboplastin preparations may adsorb thrombin and prevent it from acting on fibrinogen.

W. H. C. SHAW

1451. Estimation of Dibenamine in biological material. H. Hofmann, K. H. Boltze and D. Weyland. *Experientia*, 1955, **11** (9), 362–363.—Bromocresol purple was used as a formative element in the adduction of dyestuff to identify Dibenamine (NN-dibenzyl-2-chloroethylamine) and Dibenamine-like compounds in urine and serum. (*Cf. Anal. Abstr.*, 1956, **3**, 1095.)

R. S. TONKS

1452. Radioactive compounds excreted by rats treated with ^{35}S-labelled BAL. Preliminary studies. [Detection of BAL (dimercaprol).] B. Tamboline, A. T. Matheson and S. H. Zbarsky (Univ. British Columbia, Vancouver, B.C., Canada). *Biochem. J.*, 1955, **61** (4), 651–657.—A method is described for the detection of dimercaprol by filter-paper chromatography, with *tert.*-butyl alcohol - water as solvent and 1 per cent. aq. NiCl$_2$ as colour reagent. A brown spot, R_F 0·92, indicates the presence of dimercaprol in amounts as low as 10 to 20 μg.

J. N. ASHLEY

1453. Presence of some artefacts in the paper chromatography and electrophoresis of keto-acid phenylhydrazones extracted from biological materials. B. Mondovi, E. Antonini and G. Modiano

(Inst. Biol. Chem., University, Rome). *Ric. Sci.*, 1955, **25** (8), 2343–2350.—The formation of some artefacts derived from 2 : 4-dinitrophenylhydrazine has been shown to occur during the extraction procedures of keto acids as phenylhydrazones. Methods for the detection of these artefacts are reported. The techniques employed include paper chromatography (in either butanol - ethanol - water or *tert.*-amyl alcohol - ethanol - water) and electrophoresis, with spectrophotometric examination of the artefacts obtained. C. A. FINCH

1454. **Chromatographic separation of ATP [adenosine triphosphate] and its organic and inorganic derivatives.** P. Cerletti and N. Siliprandi (Inst. Biol. Chem., University, Rome). *Ric. Sci.*, 1955, **25** (7), 2084–2090.—A paper-chromatographic method is described for separating ATP (R_F 0·03), inosine triphosphate (0·02), inosine diphosphate (0·07), inorganic pyrophosphate (0·24), adenylic acid (0·40 to 0·37), adenosine (0·55), adenine (0·67 to 0·64) and inorganic orthophosphate (0·65 to 0·64). The R_F values are those obtained with propanol - water - trichloroacetic acid - 22° Bé aq. NH₃ (75 : 20 : 5 : 0·3). The ATP deriv. are detected by u.v. light; the inorganic phosphates by molybdic acid development. T. P. McLAUGHLIN

1455. **Paper chromatography of blood lipids and lipo-proteins and its diagnostic significance.** H. P. Kaufmann and G. Schmidt. *Fette u. Seifen*, 1955, **57** (9), 666–675.—A droplet of blood is placed on "Elphor" paper (Bender und Hobein) and the paper is dried by exposure to air for 4 to 6 hr. The chromatogram is developed at 20° C by the ascending technique with pure methanol as solvent until the solvent front has travelled 12 cm from the blood spot. Constituents of the blood that tend to separate are identified by examining the paper in ordinary and in u.v. light after it has been treated with one of the following reagents: rhodamine B for the identification and partial differentiation of fatty constituents; Sudan black B for neutral fats and phosphatides; iris blue for cholesterol; ninhydrin for protein constituents; KMnO₄ soln. for reducing substances; bromocresol green for basic substances; and glacial acetic acid saturated with benzidine for iron-containing porphyrin compounds. The emergence of a greenish-brown "tail" before the solvent front has reached a distance 12 cm from the spot generally indicates a pathological condition in the patient from whom the blood has been taken. The chemistry of the fractions separated on the chromatogram is discussed. E. HAYES

1456. **The estimation of the fatty acid composition of bacterial lipids.** K. Hofmann, C. Y. Hsiao, D. B. Henis and C. Panos (Univ. Pittsburgh, Sch. of Med., Pittsburgh, Pa., U.S.A.). *J. Biol. Chem.*, 1955, **217** (1), 49–60.—A modification of the method of Boldingh (*Brit. Abstr. C*, 1950, 325) is described for the determination of mono-unsaturated, saturated, and branched-chain fatty acids in small samples of bacterial lipids. The method involves hydroxylation of the unsaturated acids in the mixture with performic acid, and separation of the resulting mixture by reversed-phase chromatography on rubber columns. There is no distinction between oleic and *cis*-vaccenic acids; stearic and lactobacillic acids are not separated by this procedure and accumulate in the same eluate fraction. The lactobacillic acid content of this fraction is determined microbiologically with *Lactobacillus delbrueckii*. J. N. ASHLEY

1457. **Photometric determination of fatty acid ester groups in phospholipids.** M. M. Rapport and N. Alonzo (Div. Lab. and Res., New York State Dept. Health, U.S.A.). *J. Biol. Chem.*, 1955, **217** (1), 193–198.—A simple, convenient, rapid and sensitive colorimetric method is described for the determination of carboxylic ester groupings in phospholipids (<1 mg). The ester groupings interact with hydroxylamine and the resulting hydroxamic acids are determined as their coloured complexes with Fe by a spectrophotometric method, which is a modification of those described by Kornberg and Pricer (*J. Biol. Chem.*, 1953, **204**, 345) and Goddu *et al.* (*Anal. Abstr.*, 1956, **3**, 137). The method is useful for characterisation of small amounts of substances such as lecithin, lysolecithin, phosphatidyl-serine and -ethanolamine, and cardiolipin. J. N. ASHLEY

1458. **Determination of cerebrosides.** N. S. Radin, F. B. Lavin and J. R. Brown (Veterans Admin. Res. Hosp., Chicago, Ill., U.S.A.). *J. Biol. Chem.*, 1955, **217** (2), 789–796.—A colorimetric micro-method is described for the determination of cerebrosides in brain. It involves the removal of interfering lipids and non-cerebroside carbohydrate lipids by a column packed with Florisil (activated magnesium silicate) and a mixture of Duolite A-7 (a weakly basic ion-exchange resin) and Dowex 50-X4. The resulting crude cerebroside mixture is then rendered soluble by heating with 85 per cent. H₃PO₄, and the cerebrosides are determined spectrophotometrically at 625 mμ by a modified anthrone method. J. N. ASHLEY

1459. **The determination of glucosamine and galactosamine.** C. J. M. Rondle and W. T. J. Morgan (Lister Inst. of Preventive Med., London). *Biochem. J.*, 1955, **61** (4), 586–589.—A modification of the method of Elson and Morgan (*Brit. Abstr. A*, 1934, 175) is described for the determination of amino sugars. An established and rigid technique must be used; slight variations in procedure, especially those affecting the pH during the condensation with acetylacetone, cause marked differences in the colour intensity finally obtained. Glucosamine and galactosamine give identical colour intensities, and there is no significant difference between the absorption spectra of the chromophores. The colour intensities bear a linear relationship to the amount of glucosamine present over the range 5·0 to 150 μg of amino sugar. Beer's law is not obeyed when the amount of glucosamine is greater than 150 μg. Large amounts of non-nitrogenous sugars give a colour, as do urea and glyceraldehyde. The most serious errors arise in the determination of small amounts of amino sugars in the presence of large amounts of amino acids and carbohydrates. J. N. ASHLEY

1460. **A modified colorimetric method for the estimation of N-acetylamino sugars.** J. L. Reissig, J. L. Strominger and L. F. Leloir (Inst. Invest. Bioquím., Fundación Campomar, Buenos Aires, Argentina). *J. Biol. Chem.*, 1955, **217** (2), 959–966. —A modification of the method of Aminoff *et al.* (*Biochem. J.*, 1952, **51**, 379) is described. The chief alteration is the use of a conc. borate buffer instead of a carbonate buffer. The colour yield is increased about twofold, and the time required for max. colour development is decreased from 1·5 hr. to 20 min. The method is also more specific and less susceptible to factors that might interfere with colour development. With the modified method, the molar

extinction coefficient of the chromogen (based on acetylhexosamine concentration) is approx. 21,000 for N-acetylglucosamine and approx. 7,400 for N-acetylgalactosamine at the wavelength of max. absorption. A micro modification of the method enables 3×10^{-10} mole of N-acetylglucosamine to be determined.   J. N. ASHLEY

1461. Notes on the determination of amino acids by ion-exchange chromatography. J. E. Eastoe (Brit. Gelatine & Glue Res. Ass., 2a Dalmeny Av., London). *Biochem. J.*, 1955, **61** (4), 601–602.— The method of Moore and Stein (*Brit. Abstr. C*, 1949, 234; 1952, 62) for the determination of amino acids by ion-exchange chromatography is modified by using a temp. of 60° C throughout the elution of the 100-cm Dowex-50 column with acetate buffer (pH 4·25) instead of changing from 50° C to 75° C after the elution of *iso*leucine. The pH of the 0·1 M PO₄′′′ buffer used to elute the 15-cm Dowex-50 column is reduced from 6·80 to 6·75 in order to separate histidine from both lysine and hydroxylysine. The extinction of the coloured ninhydrin solutions is measured spectrophotometrically. An empirical method is given for the calculation of tyrosine values which is applicable when there is considerable overlap by phenylalanine and only a small amount of tyrosine is present.
                                                    J. N. ASHLEY

1462. Dependence of R_F values of amino acids on the shape and size of the filter-paper. H. C. Chakrabortty and D. P. Burma (Bose Res. Inst., Calcutta, India). *J. Indian Chem. Soc.*, 1955, **32** (8), 533–536.—The investigation reported shows that the R_F values of serine and valine are affected very little by the strip width or the sector angle of the filter-paper. It has been shown both experimentally and theoretically that the R_F values on strips are equal to the squares of those on sectors.
                                                    O. M. WHITTON

1463. Determination of neutral equivalents [of amino acids, etc.] by titration in alcohol. E. Ellenbogen and E. Brand (Columbia Univ. Coll. Physicians and Surgeons, New York, U.S.A.). *Anal. Chem.*, 1955, **27** (12), 2007.—Neutral equiv. of pure amino acids, peptides and peptide deriv. can be determined by titrating $\simeq 11$ ml of a soln. of the sample (2 to $10 \times 10^{-3} M$) in ethanol with 0·01 N ethanolic KOH in the presence of nitrogen and the proper indicator mixture (listed) to ensure a sharp end-point. The method is accurate to within $\pm 0·5$ per cent.; it cannot be used for guanidino deriv. Some values obtained are reported.
                                                    W. J. BAKER

1464. A micro-diffusion method for the determination of plasma glycine. T. B. Schwartz, M. C. Robertson and L. B. Holmes (Duke Univ., Durham, N.C., U.S.A.). *J. Lab. Clin. Med.*, 1955, **46** (4), 657–661.—The sample of heparinised plasma is treated with aq. picric acid, then centrifuged, and an aliquot of the clear supernatant liquid is placed in the outer chamber of a standard Conway microdiffusion unit. After evaporation to dryness, the residue is treated with ethyl phosphate and ninhydrin reagent. The formaldehyde produced is allowed to diffuse overnight into chromotropic acid reagent placed in the inner chamber of the cell. The chromotropic acid is then heated to 100° C for 30 min. and the extinction of the cooled soln. is measured at 570 mμ. Calibration is rectilinear with up to 0·12 μmole of glycine per ml, and 0·02 μmole can be determined satisfactorily. The

recovery of added glycine is 98·7 ($\pm 1·4$) per cent.
                                                    W. H. C. SHAW

1465. Comparative studies in quantitative filter-paper electrophoresis. J. R. Walsh, F. L. Humoller and A. L. Dunn (Veterans Admin. Hosp., Omaha, Nebr., U.S.A.). *J. Lab. Clin. Med.*, 1955, **46** (5), 772–780.—An evaluation is made of various factors affecting the colorimetric estimation of proteins on paper-electrophoresis patterns by subsequent treatment with a dye solution. It is concluded that reproducible results are obtainable under controlled conditions, and that within certain limits the amount of dye taken up is proportional to the amount of protein present. Direct densitometry is less satisfactory quantitatively than elution from the paper for colour measurement, and it is considered that the results obtained should be expressed in terms of percentage dye distribution rather than percentage protein distribution. If bromophenol blue is used, the wash solution should be of pH <3.
                                                    W. H. C. SHAW

1466. Analytical control of the salting-out of proteins by means of the polarographic protein reaction. V. Kalous and J. Štokr (Karlovy Univ., Prague, Czechoslovakia). *Chem. Listy*, 1955, **49** (4), 567–570.—The polarographic behaviour of proteins in Co··· soln. containing various amounts of $(NH_4)_2SO_4$ has been investigated. With an increasing concn. of the electrolyte the height of the polarographic protein wave increases, reaching its max. at a concn. of 0·3 M and then remaining practically constant. A suitable soln. for the salting-out of proteins consists of 0·001 M Co(NH₃)₆Cl₃, 0·05 M NH₄Cl, M aq. NH₃ and 0·3 M (NH₄)₂SO₄.
                                                    G. GLASER

1467. Chromatographic separation and quantitative estimation of iodine-131-labelled derivatives of sterols, amines, acids and aldehydes. W. M. Stokes, W. A. Fish and F. C. Hickey (Providence College, Providence, R.I., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1895–1898.—p-[¹³¹I]Iodobenzoic acid derivatives of sterols and amines, p-[¹³¹I]iodoaniline derivatives of acids and p-[¹³¹I]iodophenylhydrazine derivatives of aldehydes were separated chromatographically, the course of development at all stages being measured by automatic scanning of the column and recording the distribution of the γ activity. This information enabled the components of selected pairs of derivatives of the above types to be quant. determined. Recoveries of the individual components were >97·5 per cent.   G. P. COOK

1468. The use of polarography in the examination [and estimation] of ketosteroids related to cholesterol. D. M. Robertson (Queen's Coll., Dundee, Scotland). *Biochem. J.*, 1955, **61** (4), 681–688.—A standard type of recording polarograph is modified, and derivative polarography is used instead of the classical or direct method to give improved polarograms. A buffer containing 90 per cent. v/v ethanol facilitates polarography of C_{19}, C_{21} and C_{27} ketosteroids in the free state and as the betainylhydrazones. With the derivative technique, approximately 30 μg of a ketosteroid per ml can be detected and estimated (error ± 10 per cent.). Derivative polarography gives a clearer indication of the position and number of carbonyl groups in ketosteroids. The position of the half-wave potential is clearly defined, and the magnitude of the derived diffusion current maximum is much easier to determine.   J. N. ASHLEY

1469. Estimation of total free reducing plasma steroids. C. Chen, S. M. Voegtli and S. Freeman (North Western Univ. Med. Sch., Chicago, Ill., U.S.A.). *J. Biol. Chem.*, 1955, **217** (2), 709–719.— A simple and reproducible method is described for the determination of total free reducing cortico-steroids in plasma. The plasma is extracted with methylene dichloride, and the residue from the washed and dried extract is dissolved in a suitable solvent, applied to filter-paper, and subjected to repeated ascending chromatography with *n*-hexane and methanol. The steroids are located at the methanol front, which is cut out and extracted, and the steroids are determined colorimetrically or spectrophotometrically by the blue tetrazolium method; other methods may also be used. The main interference is probably due to Δ^4-3-keto and 17α-hydroxy-20-keto compounds, which are not completely removed from the extract during the subsequent operations. One analyst can carry out 24 determinations in two days. J. N. ASHLEY

1470. Paper chromatography of steroid glucurono-sides and sulphates. M. L. Lewbart and J. J. Schneider (Jefferson Med. Coll., Philadelphia, Pa., U.S.A.). *Nature*, 1955, **176**, 1175–1176.—Three solvent systems, *n*-butyl acetate - *n*-butanol - 10 per cent. acetic acid, *n*-butyl acetate - *n*-butanol - 10 per cent. formic acid, and *n*-butyl acetate - methanol - 0·1 M sodium barbitone buffer in 50 per cent. aq. methanol, were used. The R_F values of the conjugates, β-cortolone monoglucuronoside, tetrahydrocortisone monoglucuronoside, dehydro-*epi*androsterone glucuronoside, pregnanediol mono-glucuronoside, sodium dehydro*epi*androsterone sul-phate, sodium androsterone sulphate, and sodium pregnenolone sulphate, are tabulated.

O. M. WHITTON

1471. Manometric determination of cocarboxylase. V. Boffi, A. Lucarelli and E. Bucci (Inst. Biol. Chem., University, Rome). *Ric. Sci.*, 1955, **25** (7), 2069–2076.—The manometric determination of cocarboxylase is rendered more accurate by using as co-enzyme a phosphatase-free *apo*carboxylase solution. This is prepared by incubating dried yeast (25 g) in 100 ml of $M/15$ phosphate buffer at pH 7·2 for 3 or more hours at 37° C. The suspen-sion is diluted with 50 ml of water to assist partition and centrifuged (4000 rev. in 20 min. at 0° C). The supernatant liquid is cleared with 20 ml of 0·5 M phosphate buffer (pH 7·2) and 7 ml of M calcium acetate, and centrifuged (4000 rev.), and the ppt. is washed with 60 ml of water. The combined supernatant solutions are pptd. with 38 g of $(NH_4)_2SO_4$ for each 100 ml, cooled at 0° C for 10 min. and centrifuged. The ppt. is redissolved in 60 ml of 0·1 M citrate buffer at pH 6, repptd. as before with $(NH_4)_2SO_4$, and this ppt. is suspended in 12 ml of satd. $(NH_4)_2SO_4$. From this carboxylase solution, which is stable for at least 1 month, *apo*carboxylase is prepared by adding 4 ml of water to 2 ml of suspension, followed by 9 ml of satd. $(NH_4)_2SO_4$ and 1 drop of conc. aq. NH_4, and centri-fuging (15,000 rev. in 3 min. at 0° C). This pro-cedure is repeated and the final ppt. is dissolved in 5 ml of 0·1 M citrate buffer at pH 6. Curves are given for the production of CO_2 from Na pyruvate with (in this case) 0·2 ml of *apo*carboxylase solution added to 0·1 to 1·0 μg of cocarboxylase, and also of the breakdown of the cocarboxylase into the mono-phosphoric ester, using unpurified yeast extracts, and consequent reduction in CO_2 readings.

T. P. McLAUGHLIN

1472. Studies in detoxication. LXVII. The biosynthesis of the glucuronides of umbelliferone and 4-methylumbelliferone and their use in fluorimetric determination of β-glucuronidase. J. A. R. Mead, J. N. Smith and R. T. Williams (St Mary's Hosp. Med. Sch., London). *Biochem. J.*, 1955, **61** (4), 569–574.—4-Methylumbelliferone glucuronide is readily prepared by biosynthesis and is used as a substrate in a very sensitive fluorimetric method for the determination of β-glucuronidase. It is itself practically non-fluorescent, but is hydrolysed to the intensely fluorescent hydroxycoumarin, of which 0·01 μg per ml or less can be determined fluorimetri-cally. The material or tissue to be assayed is ground with sand or disintegrated in a glass homo-geniser, and the solution is incubated with the glucuronide in acetate buffer (pH 4·6) at 37° C for 0·5 hr. The fluorescence is measured against a quinine bisulphate standard. J. N. ASHLEY

1473. Chitinase in some Basidiomycetes. [Determ-ination of chitinase.] M. V. Tracey (Rothamsted Exp. Sta., Harpenden, Herts., England). *Biochem. J.*, 1955, **61** (4), 579–586.—Methods for the visco-metric and hydrolytic assay of chitinase are des-cribed. In the viscometric method the decrease in viscosity of a chitosan solution with time is determined after addition of the enzyme solution. In the hydrolytic assay the amount of acetylglucos-amine produced from chitin by the enzyme solution is determined. J. N. ASHLEY

1474. Chemical evaluation of the functions of the liver. J. G. Reinhold (Hosp. Univ. Pennsylvania, Philadelphia, U.S.A.). *Clin. Chem.*, 1955, **1** (6), 351–421.—A review with 437 references.

H. F. W. KIRKPATRICK

See also Abstracts 1250, 1288, 1297, 1488, 1494, 1504, 1509, 1539, 1545, 1547, 1582.

Drugs

1475. Identification of simple drugs and control of vegetable medicaments by paper chromatography. R. Paris and J.-P. Viejo (Fac. Pharm. Paris, Lab. Matière Méd.). *Ann. Pharm. Franç.*, 1955, **13** (6), 424–430.—Extracts of vegetable drugs are made and, usually without further concentration, are chromatographed with *n*-butanol - acetic acid - water (4:1:5) saturated at a temp. not above 15° to 18° C. Suitable methods of detecting the spots on the chromatogram and R_F values (approx.) are given. Results with substances used as adulterants are quoted. E. J. H. BIRCH

1476. Polarographic determination of atropine in mixtures. B. Novotný (State Inst. for Control of Drugs, Prague, Czechoslovakia). *Českosl. Farmac.*, 1955, **4** (9), 448.—Atropine (**I**) is extracted from alkaline solution with chloroform, which is evapor-ated off, and the **I** is nitrated with HNO_3 - H_2SO_4 mixture ($>10:1$) on a water bath for 30 min. The mixture is made alkaline and, after removing oxygen by means of nitrogen, polarography of the soln. is carried out. The polarogram is compared with one prepared from a similar sample to which a known amount of atropine is added. Calibration curves are given. The method is accurate and suitable for the determination of **I** in the presence of a large excess of morphine or nicotinic acid.

A. O. JAKUBOVIC

1477. A fluorimetric assay of reserpine. E. B.
Dechene (C. E. Frosst Co., Montreal, Canada).
J. Amer. Pharm. Ass., Sci. Ed., 1955, **44** (11), 657–
660.—The fluorescent intensity of reserpine soln.
when heated with H_2O_2 soln. increases 10-fold over
untreated soln. and is quant. related to the alkaloid
concn. *Procedure*—Duplicate aliquots of the reser-
pine soln., estimated to contain 1 μg of reserpine,
are placed in suitable cuvettes containing 1 ml of a
3 per cent. H_2O_2 soln. and the vol. is made up to
10 ml with 5 N acetic acid. The soln. is heated in a
boiling-water bath for 45 min., then cooled, and the
fluorescence under u.v. light is determined at
25° C. Standard curves are not employed, since
greater accuracy is attained by the simultaneous
measurement of known and unknown soln., the
known soln. containing 1 μg of reserpine in 5 ml of
5 N acetic acid. Concn. of 0·2 μg of reserpine in
10 ml of soln. are measurable. The method has been
adopted for the determination of reserpine in
powdered extract of *Rauwolfia serpentina* and for
tablet assays.   G. R. WHALLEY

**1478. The determination of reserpine by chromato-
graphic separation from pharmaceutical products.**
W. F. Bartelt and E. E. Hamlow (Upjohn Co.,
Kalamazoo, Mich., U.S.A.). *J. Amer. Pharm. Ass.,
Sci. Ed.*, 1955, **44** (11), 660–662.—A simple method
for determining reserpine in pharmaceutical prod-
ucts is described, which gives a result within
approx. 2·5 per cent. of the amount present.
Procedure—A column (2 cm × 20 cm) is packed
with a 1 : 1 mixture of Solka-floc and Celite in water,
and the column is then washed with 50 ml of 5 N
acetic acid followed by 50 ml of 50 per cent. ethanol.
The reserpine sample, made up to contain 0·5 mg
per 10 ml of a methanol - acetic acid soln., having a
pH of 2·5 to 6·0 and an ethanol content below 30
per cent., is applied to the column, followed by
100 ml of water in 15-ml quantities. The column
is further washed with 30 ml of 27 per cent. ethanol,
followed by 50 ml of water; the reserpine is then
eluted with 60 ml of 5 N acetic acid, which is
collected, and the absorption is measured at
267 mμ.   G. R. WHALLEY

1479. Reserpine from *Alstonia constricta*. R. G.
Curtis, G. J. Handley and T. C. Somers (Nicholas
Pty Ltd., Melbourne, Australia). *Chem. & Ind.*,
1955, (49), 1598–1599.—The dried root bark (500 g)
was ground and exhaustively extracted with warm
(40° C) 90 per cent. ethanol in an atmosphere of N.
The ethanolic extracts were concentrated to 500 ml
under vacuum, diluted with 1 per cent. phosphoric
acid (500 ml) and the solution was extracted with
$CHCl_3$. Free weak bases are extracted, and the
stronger bases remain in the aqueous phase. The
residue after evaporation of $CHCl_3$ was washed
with cold light petroleum and then dissolved in
warm ethanol (50 ml). The soln. was set aside
overnight, when an orange powder (0·15 g), m.p.
260° C, which appears to be an alkaloid salt, was
filtered off and washed with cold ethanol. The
filtrate was evaporated to dryness under vacuum,
the residue was dissolved in $CHCl_3$, and the soln.
was passed down an alumina column (100 g),
eluting with $CHCl_3$. Reserpine was associated
with a trace of yellow material in the leading band.
The crystalline material isolated (0·25 g) had m.p.
263° to 265° C (open tube) and $[\alpha]_D^{23} - 120°$
($CHCl_3$). From the weak base fraction, another
alkaloid, m.p. 184° to 185° C, has been isolated.
Its ultra-violet absorption spectrum is described.
                    O. M. WHITTON

**1480. The chromatographic analysis of reserpine
preparations.** D. Banes, J. Carol and J. Wolff
(Div. Pharm. Chem., F. & D.A., Dept. Health,
Educ. and Welfare, Washington, D.C., U.S.A.).
J. Amer. Pharm. Ass., Sci. Ed., 1955, **44** (10),
640–644.—A paper-chromatographic method is
described for the detection of reserpine and its
separation from closely related alkaloids, and a
liquid - liquid partition method for its determina-
tion. In the quant. method the adsorbent is
Celite 545, the stationary solvent is a soln. of citric
acid in dil. ethanol and the eluent is chloroform - *iso*-
octane satd. with water. The extinction of the
eluate is measured at 268 mμ and the reserpine
calculated by comparison with a standard. Weights
of ≃2 mg of reserpine can be determined with
satisfactory accuracy.   G. R. WHALLEY

1481. The determination of protoveratrine. J.
Levine and H. Fischbach (F. and D.A., Dept.
Health, Educ. and Welfare, Washington, D.C.,
U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1955,
44 (12), 713–716.—Protoveratrine A (**I**) can be
quant. separated from protoveratrine B (**II**) by
partition chromatography on Celite, and determined
colorimetrically by complexing with chlorophenol
red (**III**). *Separation*—Moisten Celite (1 g) with
a mixture (2 : 1) (1 ml) of buffer, pH 3·5, and ethylene
glycol and pack in a column. Add a soln. of the
sample (2 mg) in benzene (5 to 10 ml). Elute the
I with benzene (200 ml) and the **II** with 1 : 2-di-
chloroethane (150 ml). Evaporate the eluates to
dryness and dissolve each residue in $CHCl_3$ (10 ml).
Determination—Moisten Celite (1 g) with a mixture
(4 : 2 : 3) (1 ml) of 0·1 per cent. **III** in the buffer,
ethylene glycol and 95 per cent. ethanol, pack in a
column and wash with H_2O-saturated $CHCl_3$ (10
ml). Add a 1-ml aliquot of a $CHCl_3$ soln. of the
sample, elute with $CHCl_3$ (3 ml then 7 ml) and collect
in N Na_2CO_3 (5·0 ml). Shake well, clarify the aq.
layer by centrifuging, and determine the extinction
at 575 mμ. Carry out a blank determination.
                    A. R. ROGERS

**1482. Paper-chromatographic method for determin-
ing alkaloids in tobacco.** R. N. Jeffrey and W. H.
Eoff (Agric. Res. Service, U.S. Dept. Agric., Belts-
ville, Md., U.S.A.). *Anal. Chem.*, 1955, **27** (12),
1903–1905.—A chromatographic method is des-
cribed for the individual determination of nicotine,
nornicotine and anabasine in tobacco. The com-
ponents are detected on the paper by treatment with
cyanogen bromide; nicotine produces a yellow spot,
$R_F \simeq 0.6$, anabasine a yellow spot, R_F 0·16, which
eventually turns pink, and nornicotine a yellow
spot, R_F 0·10. A quant. determination within
10 per cent. can be made by visual examination of
the spots, the results being most reliable in the
range 2 to 4 μg. The limit of detection is ≃0·25 μg.
Comparison with other methods is made.
                    G. P. COOK

**1483. The analysis of solutions of epinephrine
[adrenaline] and norepinephrine [noradrenaline].**
L. H. Welsh (Food and Drug Admin., Washington,
D.C., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*,
1955, **44** (8), 507–514.—Dilute aq. soln. of adrenaline
(**I**) and noradrenaline (**II**) are quant. estimated by
the formation of their triacetyl deriv. and the polari-
metric examination of the products. **I** and **II** in
soln. containing 0·5 per cent. of chlorobutanol and
0·1 per cent. of $NaHSO_3$ are extracted 3 times with
25-ml portions of CCl_4 to remove the chlorobutanol.
Starch soln. is then added, dropwise, and the

$NaHSO_3$ is destroyed by the addition of I and KI until a blue colour just persists, which is then discharged with $0.1 N Na_2S_2O_3$. To this soln. are added 2.1 g of $NaHCO_3$ followed by 1 ml of acetic anhydride, and the soln. is rapidly shaken in a separating funnel until the evolution of CO_2 has ceased, when it is allowed to stand for 5 min. before being extracted with six 30-ml portions of $CHCl_3$. The combined extracts are filtered, evaporated to dryness and heated at 105° C for 30 min., when the residue is weighed and dissolved in 5 ml of $CHCl_3$; the optical rotation of the resulting soln. is determined in a 200-mm polarimeter tube, whence the amounts of I and II are calculated. The triacetyl deriv. of I and II can be adsorbed chromatographically on a Celite column from water-satd. benzene and the triacetyl deriv. of II is eluted with $CHCl_3$. For the colorimetric determination of II, its triacetyl deriv. is dissolved in 5 or 10 ml of $0.5 N$ HCl. The soln. is warmed in boiling water for 5 min., then heated at 100° C for 30 min. in a stoppered tube. A 0.5 to 1-ml aliquot of the cooled soln. is neutralised with a $NaHCO_3$ soln. (42 mg per ml) and the vol. is adjusted to 2.5 ml, then 2.5 ml of a buffer soln., pH 6, are added followed by 4 drops of $0.1 N$ I soln. After 3 min., 6 drops of $0.1 N Na_2S_2O_3$ soln. are added, and the extinction of the final soln. is measured at 520 mμ, 3 min. ($\pm$30 sec.) after the addition of the $Na_2S_2O_3$, the resulting values being compared with a previously standardised curve.

G. R. WHALLEY

1484. A further note on the gravimetric determination of santonin. N. A. Qazilbash (Islamia Coll., Peshawar, Pakistan). *J. Pharm. Pharmacol.*, 1956, **8** (1), 27–32.—The method previously reported (*Brit. Abstr. C*, 1951, 264; *J. Pharm. Pharmacol.*, 1952, **4**, 511) for the gravimetric assay of artemisia has been modified. The dried benzene extract is heated with $Ba(OH)_2$ soln. on a steam bath; a stoppered flask is used in place of a crystallising dish. A correction factor of 6.4 mg per 10 ml of filtrate is added to the final weight of santonin obtained. This modified method is preferred to the procedure of Kassner, Johnson and Terry (*Brit. Abstr. C*, 1953, 398). (See *Anal. Abstr.*, 1956, **3**, 1485.)

A. R. ROGERS

1485. The assay of artemisia. E. W. Kassner, C. A. Johnson and N. A. Terry (90 Greenhill, Hampstead, London, England). *J. Pharm. Pharmacol.*, 1956, **8** (1), 71–72.—This is a commentary on the criticisms of Qazilbash (*Anal. Abstr.*, 1956, **3**, 1484).

N. E.

1486. The analysis of conjugated oestrogen preparations. P. M. Sanders, D. Banes and J. Carol (F. and D.A., Dept. Hlth, Educ. and Welfare, Washington, D.C., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** (12), 727–730.—Two methods are proposed for the hydrolysis of conjugated oestrogens: (*A*) by boiling the sample ($\equiv$ 5 mg of free oestrogens) with HCl (1 ml) and methanol (25 ml) for 5 min.; (*B*) by trans-esterification to the acetate, with acetic anhydride in pyridine, and hydrolysing by simmering with 10 per cent. aq. Na_2CO_3 (5 ml) for 30 min. Recoveries are higher than by hydrolysis with aq. HCl or with trichloroacetic acid in dioxan. The methods have been applied to the assay of pharmaceutical preparations (such as tablets).

A. R. ROGERS

1487. Methods for the application of periodate oxidation to the analytical control of chloramphenicol. A. Valseth and A. Wickstrøm (Univ. Oslo, Norway). *Medd. Norsk Farm. Selsk.*, 1955, **17**

(11), 345–355.—An indirect volumetric assay method described for chloramphenicol (**I**) is based on the periodate oxidation of D-(−)-*threo*-2-amino-1-*p*-nitrophenyl propane-1:3-diol (**II**), which is liberated by hydrolysis of **I**. The optimum pH for the oxidation is from 7.0 to 7.5. Quantities above 0.2 per cent. of the biologically inactive **II** in **I** have been determined quantitatively by oxidation with periodate and spectrophotometric determination of liberated NH_3 after separation from the mixture by micro-diffusion. With no other periodate-reducing compound present, **II** can be determined in **I** by direct titration with periodate. O. M. WHITTON

1488. Polarography of chloramphenicol and related compounds. E. Knobloch and E. Svátek (Pharm. Biochem. Res. Inst., Prague, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1955, **20** (5), 1113–1124.—The reduction curves of chloramphenicol (**I**) and some of its decomposition products [2-amino-1-*p*-nitrophenyl propane-1:3-diol (**II**), α-dichloroacetamido-β-hydroxyethyl *p*-nitrophenyl ketone (**III**), α-dichloroacetamidovinyl *p*-nitrophenyl ketone (**IV**)] in Britton-Robinson buffers at pH 2.2, 4.0, 5.5, 7.0 and 10.0 are given. The effect of gelatin and thymol as maximum suppressors are studied. It is found that gelatin causes the reduction potential to become more negative; a concn. >0.0025 per cent. should not be used. At pH 2.2 the chloramphenicol curve shows three steps. It is demonstrated, by reference to other compounds, that these steps are due to the reduction of the nitro group to hydroxylamine, of the hydroxylamine to the amine and to reduction of the dichloroacetyl group. Polarograms of **II**, **III** and **IV** are similarly studied and explained. Impurities found in racemic **I** having a ketone group *para* to the nitro group, *e.g.*, **III** and **IV**, can be quant. estimated and qual. distinguished in the presence of a two-hundred-fold excess of **I**. A method for estimating **I** in blood and urine at a concn. of 0.01 mg per ml is given. P. S. STROSS

1489. New simple method for the qualitative and quantitative determination of small quantities of 4-aminosalicylic acid. Yu. M. Ostrovskii. *Aptechnoe Delo*, 1955, **4** (6), 10–13.—4-Aminosalicylic acid (**I**) can be detected by means of the intense orange-brown colour formed when it is oxidised with $K_3Fe(CN)_6$ in alkaline soln. *Procedure*—To 2 ml of a soln. containing 0.005 to 0.05 per cent. of **I** add 0.6 ml of a freshly prepared mixture of a 33 per cent. soln. of NaOH (15 ml) and a 2 per cent. soln. of $K_3Fe(CN)_6$ (35 ml). Measure the colour within 15 min. in an absorptiometer and calculate the content of **I** by means of a calibration curve constructed with a standard soln. of **I**. Salicylic acid, acetylsalicylic acid, phenazone, acetanilide, sulphanilamide, sulphapyridine, sulphacetamide, benzocaine and nikethamide in concn. of less than 0.1 per cent. do not interfere. The colour is stable for 15 to 20 min.; it can be made stable for 12 hr. by adding ascorbic acid, but this reduces its intensity. E. HAYES

1490. Use of some aldehydes for the identification of 4-aminosalicylic acid. A. M. Gal'perina (N.I. Pirogov Med. Inst., Odessa). *Aptechnoe Delo*, 1955, **4** (6), 8–10.—When 0.1 g of hexamine and 2 ml of conc. H_2SO_4 are added to 0.1 g of 4-aminosalicylic acid (**I**) at 15° to 20° C, a green colour is produced which changes first to orange and then to orange-red. The reaction can be used to detect **I**. Salicylic acid, benzocaine, procaine, *p*-aminobenzoic

acid and various sulphonamides give no colour with the reagent; phenol, o-aminophenol, p-aminophenol, aniline, Rivanol (2:5-diamino-7-ethoxyacridine lactate) and o-sulphanilylaniline give different colours; m-aminophenol gives the same colour as **I**. Formaldehyde soln. or butyraldehyde can be used instead of hexamine and H_2SO_4 to detect **I**, but they are less satisfactory.   E. HAYES

1491. Quantitative determination of sodium 4-aminosalicylate. M. S. Baron. *Aptechnoe Delo*, 1955, **4** (5), 17–19.—Three methods for determining Na 4-aminosalicylate (**I**) are described. (*i*) Ether (25 ml) is added to 20 to 25 ml of $\simeq 0.1\ N$ soln. of **I** and the soln. is titrated against $0.1\ N$ HCl soln., with methyl orange as indicator, until the colour of the aq. layer changes. (*ii*) A weighed sample of **I** (0.4 to 0.5 g) is dissolved in 10 to 20 ml of water in a 50-ml calibrated flask; 5 ml of a 10 per cent. soln. of $CuSO_4$ are added, and the mixture is made up to 50 ml and set aside for 10 to 15 min. The soln. is filtered and the Cu in an aliquot of the filtrate is determined iodimetrically. A blank experiment is also carried out. (*iii*) A two-fold excess of $0.1\ N$ $AgNO_3$ soln. is added to 10 to 20 ml of $\simeq 0.1\ N$ soln. of **I** in a 50-ml calibrated flask. The mixture is made up to 50 ml, shaken and set aside for 10 min. The soln. is filtered and the excess of $AgNO_3$ in an aliquot of the filtrate is determined by Volhard's method.   E. HAYES

1492. The identification of antihistaminic agents. A. Osol and C. N. Sideri (Philadelphia Coll. Pharm. and Sci., Pa., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** (12), 761–762.—The characteristic reactions of 11 antihistamines on mixing the sample (25 mg) with conc. H_2SO_4 (5 ml), before and after dilution with H_2O (20 ml), serve to differentiate and identify them. Antazoline and chlorpheniramine remain colourless with H_2SO_4, but only the former gives a deep-red colour with HNO_3.
                A. R. ROGERS

1493. Ultra-violet absorption spectra of antihistaminic agents. L. J. Kleckner and A. Osol (Philadelphia Coll. Pharm. and Sci., Pa., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** (12), 762–765.—The u.v. absorption spectra of the following U.S.P. antihistamines—antazoline hydrochloride, chlorcyclizine hydrochloride, chlorothen citrate, methapyrilene hydrochloride, phenindamine tartrate, pyrilamine maleate, thenyldiamine hydrochloride and tripelennamine hydrochloride—have been determined in water at pH 0.1, 2.0, 4.1 and 5.7, and in ethanol. Ethanol is preferred to water for the extraction of these drugs from tablets before spectrophotometric assay.   A. R. ROGERS

1494. Descending chromatographic behaviour and differentiation of some antihistamines and alkaloids. Q. C. Belles and H. W. Sievert (Army Med. Lab., Fort Lewis, Washington, U.S.A.). *J. Lab. Clin. Med.*, 1955, **46** (4), 628–640.—One-dimensional descending chromatography is on Whatman No. 4 paper with (*i*) n-butanol saturated with N HCl, (*ii*) n-butanol containing 10 per cent. v/v of N HCl and (*iii*) n-butanol saturated with phosphate buffer, pH 6.5. R_F values with each solvent are given for 11 antihistamines and for 16 common alkaloids with which they may be confused if conventional alkaloidal spot-tests are used. Identification of individual compounds on the chromatograms is by fluorescence in u.v. radiation before and after treatment with cyanogen bromide and by

colours developed on further treatment with ethanolic benzidine. Differentiation from alkaloids is by the use of a $K_3Fe(CN)_6$ - $FeCl_3$ spray reagent and by u.v. absorption. Details are given for preparing tablets, powders, urine, blood and tissue homogenates for chromatography.
                W. H. C. SHAW

1495. Polarographic determination of azo compounds as active ingredients of ointments. G. Dušínský and Z. Gruntová (State Inst. for Control of Drugs, Bratislava, Czechoslovakia). *Českosl. Farmac.*, 1955, **4** (9), 445–448.—The polarographic determination of 4-diacetylamino-2′:3-dimethylazobenzene (Pellidol) (**I**), sodium 4-sulphomethylamino-2′:3-dimethylazobenzene (Epitegin) (**II**), and (2-methyl-4-o-tolylazophenylazo)hydrocupreine (Interazin) (**III**) is described. They are extracted from the ointment by 50 per cent. acetic acid and the polarography is carried out in about 2.5 N acetic acid. For **I**, 25 per cent. ethanol and (as buffer) sodium acetate (0.5 M) are also present. The height of the polarographic wave is proportional to the azo-compound content in the concn. region of 1×10^{-4} to $1 \times 10^{-5}\ M$ for **I** and 1×10^{-4} to $5 \times 10^{-4}\ M$ for **II**. Since **III** gives two waves the sum has to be taken; then the same relationship holds for concn. of 1×10^{-4} to $5 \times 10^{-4}\ M$. The second wave has a characteristic max., which can be removed by the addition of fuchsine. The method is rapid (40 to 60 min.) and accurate; ointment bases do not interfere.
                A. O. JAKUBOVIC

1496. A spectrophotometric assay of terpin hydrate. H. Platt and A. E. James (Temple Univ., Philadelphia, Pa., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** (11), 666–668.—A spectrophotometric assay of terpin hydrate applicable to proprietary products is described, which depends on the coloration produced with molybdophosphoric acid in the presence of H_2SO_4. The extinction of this soln. is determined at 660 mμ, and compared with similarly treated blanks, the terpin hydrate content being determined by comparison with reference standards.   G. R. WHALLEY

1497. Polarographic determination of ionic copper present in the commercially available copper chlorophyllins. W. L. Wuggatzer and J. E. Christian (Purdue Univ., Lafayette, Ind., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44**, (10), 645.—Known quantities of dried $CuSO_4$ are dissolved in 1.5 M aq. NH_3 - NH_4Cl soln. and the soln. is electrolysed at the dropping electrode. A graph is plotted of corrected diffusion currents against concn. of Cu; a straight line is obtained. Known concn. of Cu chlorophyllins are similarly electrolysed, and the content of Cu is determined from the standard graph. The concn. of ionic Cu present in commercial products ranges from 0.17 to 1.35 per cent.
                G. R. WHALLEY

1498. The assay of sodium radio-iodide (^{131}I) used for medicinal purposes. J. J. Pinajian and J. E. Christian (Purdue Univ., Lafayette, Ind., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** (10), 631–636.—An analytical procedure is described for the determination of ^{131}I that is to be used medicinally. *Procedure*—The activity of ^{131}I is calibrated by the use of an absolute beta-counting method with a collimated Geiger - Müller tube, or by using a synthetic standard for ^{131}I, similar in beta energy to the spectrum of ^{131}I and which can be used as a reference standard, or alternatively,

with a standard calibrated sample of ^{131}I. A secondary calibration of ^{131}I activity is then determined with a quartz-fibre electroscope, when the characterisation of the beta radiation is determined from the mass-absorption coefficient in Al. The final chemical analysis is achieved by ascending paper-chromatography, in which 1-μg quantities of ^{131}I soln. are spotted on to the paper and dried with similar quantities of standard reference soln., containing 1·66 mg of KI, 2·14 mg of KIO$_3$ and 10 mg of NaHCO$_3$ per ml, and the chromatograms are developed with 75 per cent. methanol soln. An automatic scanning device and recording apparatus are used to determine the activities of iodide and iodate, and a planimeter is used to determine the ratio of iodide to iodate activity. R_F values of 0·76 and 0·45 were obtained for iodide and iodate, respectively. G. R. WHALLEY

1499. Determination of iron salts present as impurities in zinc and copper (pharmaceutical) preparations. Ts. I. Shakh. *Aptechnoe Delo*, 1955, **4** (5), 13–17.—For preparations of Zn, a weighed sample (0·1 to 0·3 g) is dissolved in 5 to 10 ml of water or 3 to 4 ml of dil. HCl soln. in a 50-ml calibrated flask; 5 ml of sulphosalicylic acid soln. (10 g of sulphosalicylic acid + 20 g of hexamine + water to 100 ml) and 25 ml of a buffer soln. (100 ml of 6 N HCl soln. + 380 ml of 50 per cent. Na acetate soln.) are then added and, after being thoroughly mixed, the contents of the flask are made up to 50 ml. The flask is set aside for 1 hr. and the colour of the soln. is measured in an absorptiometer with a yellow filter. The iron content is calculated from a calibration curve constructed with a standard soln. of Fe(NO$_3$)$_3$.9H$_2$O. A blank determination allows for Fe in the reagents. For preparations of Cu, the Cu is pptd. with metallic Zn and the Fe in the solution is determined in the same way as for zinc preparations. The precision is ±10 per cent. E. HAYES

1500. Quantitative determination of bivalent iron preparations containing organic substances. F. E. Kagan (Kiev Post-grad. Med. Inst.). *Aptechnoe Delo*, 1955, **4** (5), 10–13.—Two methods are described for the determination of Fe^{II} in pharmaceutical preparations. In the first method, a weighed sample of the preparation (dissolved in water if soluble) is treated with an excess of 0·1 N ICl or ICl$_3$ soln. and, after the addition of K Na tartrate and an excess of KI, the liberated iodine is titrated against 0·1 N Na$_2$S$_2$O$_3$. In the second method, which is suitable for preparations containing oxidising agents, the sample is dissolved in H$_2$O or dil. HCl soln. and an excess of 0·1 N ICl soln. is added; the liberated iodine is extracted with chloroform and titrated against 0·1 N Na$_2$S$_2$O$_3$. The methods are applied to the pharmacopoeial (U.S.S.R. VIII) preparations ferrous lactate, saccharated iron carbonate and syrup of ferrous iodide.

E. HAYES

1501. Compleximetric titrations in pharmaceutical analysis. XIII. Determination of bismuth. V. Suk, O. Koldinsky and M. Malát (Inst. Anal. Chem., Karlovy Univ., Prague, Czechoslovakia). *Československ. Farmac.*, 1955, **4** (9), 449–451.—Catechol violet forms an intensely blue complex with bismuth at pH >2. On titrating a bismuth soln. with EDTA (disodium salt) in the presence of this indicator the colour of the soln. changes sharply to yellow at the equivalence point. If the original soln. is violet instead of blue it is too acid and should be adjusted to a pH of 2 to 3 with aq. NH$_3$. The method is applied to a number of inorganic and organic bismuth compounds, the error for the former being <0·4 per cent. and for the latter <±1 per cent. Among the compounds examined were basic bismuth gallate, iodogallate, salicylate and tribromophenoxide. The organic matter was destroyed before the titration by heating with HNO$_3$ and H$_2$O$_2$. A. O. JAKUBOVIC

1502. A non-aqueous titration assay for sodium carboxymethylcellulose. C. N. Sideri and A. Osol (Philadelphia Coll. Pharm. and Sci., Pa., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** (12), 759–760.—Sodium carboxymethylcellulose can be assayed by heating the sample (500 mg) for 20 min. with glacial acetic acid (80 ml) on a boiling-water bath, cooling to room temp. and titrating with 0·1 N perchloric acid in dioxan. The results are slightly lower than by the copper precipitation method, unless the organic matter is destroyed by ignition before titration. The determination of sulphated ash gives high results. A. R. ROGERS

1503. Production control of polyelectrolyte parenterals with a flame photometer. H. Hershenson and D. F. Smith (Don Baxter, Inc., Glendale, Calif., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** (12), 731–735.—Quantitative determinations of Na, K and Ca, and semi-quant. determinations of Mg in parenteral soln. can be performed accurately and economically by comparison with standard soln., with a flame photometer; Na and K mutually enhance their luminosities. Less than 6 per cent. of dextrose hydrate does not affect alkali-metal luminosity at the 100 p.p.m. level. The alkaline-earth metals require larger slit widths compared with the alkali metals, but the calibration curves are linear. Sodium and potassium enhance, and lactate depresses, calcium luminosity. Dextrose greatly enhances alkaline-earth luminosity, but a correction factor can be applied in routine analysis to avoid the difficulty of storing a standard dextrose soln.

A. R. ROGERS

See also Abstracts 1400, 1527, 1529, 1530, 1531.

Food

1504. Determination of amino acids in food products by means of chromatography on starch columns. H. Kraut, E. Kofrányi, H. Telschow and M. Weber (Max-Planck Inst., Dortmund, Germany). *Hoppe-Seyl. Z.*, 1955, **301** (4–6), 165–184.—Moore and Stein's method for the analysis of amino acids by chromatography on starch columns (*Brit. Abstr. C*, 1949, 234, 343) was investigated for use as a routine method and some modifications were introduced, e.g., German potato starch of 12 to 17 per cent. moisture content, mixed with *isobutyl* alcohol, was used as filler to give columns with a time of flow of 50 to 60 min. at 120 mm pressure. Mixtures of *n*-propanol, *n*-butanol and 0·1 N HCl (2:1:1) followed by *n*-propanol and 0·5 N HCl (3:2) were used as eluting agents and Boissonas reagent (*Brit. Abstr. C*, 1951, 415), containing 12·5 mg of ninhydrin, buffered by Na acetate, as colour developer. Extinctions were measured in an Eppendorf photometer at 578 mμ (proline at 436 mμ). The process was tested on synthetic mixtures of amino acids, on hydrolysates of casein, milk, two types of wheat flour and barley. Results show a mean deviation of ±4·5 per cent. as compared with microbiological values for the respective

amino acids. The sum of nitrogen contents for a synthetic mixture of 13 amino acids was 100·9 per cent.; a loss of 2 to 5 per cent. of nitrogen was found in hydrolysates of casein and milk, and 5 to 10 per cent. in wheat flour and barley. An explanation for this deficiency is suggested.

S.C.I. ABSTR.

1505. Determination of benzoic and salicylic acids in food products. D. T. Englis, B. B. Burnett, R. A. Schreiber and J. W. Miles (Carothers Res. Lab. Exp. Sta., E.I. du Pont de Nemours & Co., Wilmington, Del., U.S.A.). *J. Agric. Food Chem.*, 1955, **3** (11), 964–969.—The acids are generally extracted, with an org. solvent, from an aq. solution acidified with HCl. On spectrophotometric examination in ether solution, benzoic and salicylic acids have absorption peaks at 227 and 236 mμ, respectively; salicylic acid has a secondary max. near 306 mμ. With this method benzoic acid has been determined in samples of ketchup and orange-base concentrate. The benzoate may be extracted directly from margarine samples with dil. NaOH, the extract being clarified with alumina cream. Quantitative determinations involve careful consideration of the solvent and the pH of the solutions.

S.C.I. ABSTR.

1506. The determination of crude fibre. V. V. P. Hirsjärvi (Staatlich. agrikulturchem. Lab., Helsinki, Finland). *Z. anal. Chem.*, 1955, **148** (3), 187–191.—Comparison of five methods for the determination of the crude fibre content of 15 samples of cereal products indicates that the best results are obtained by Hirsjärvi and Andersen's modification (*Anal. Abstr.*, 1954, **1**, 1648) of the method of Puranen and Tomula. A. R. ROGERS

1507. Rapid and simple method of invert-sugar determination. S. Nikiel. *Gaz. Cukr.*, 1955, **57**, 91–92.—The method, based on that of Main (*Int. Sugar J.*, 1932, **34**, 213, 460), is for the determination of reducing sugars present up to 0·3 per cent. in other sugars, and involves the reduction of $K_3Fe(CN)_6$, with methylene blue as indicator. Stock soln. are prepared as follows—(*a*) 0·1 g of methylene blue dissolved in 250 ml of hot water, with 20 g of anhydrous K_2CO_3, and made up to 500 ml; (*b*) 5 g of $K_3Fe(CN)_6$ dissolved in 250 ml of water and made up to 500 ml; a mixture of equal volumes of (*a*) and (*b*) is made as required. The sugar (25 $\pm$ 0·1 g) is weighed into a 300-ml flask; a piece of pumice is mixed with $CaCO_3$ and 50 ml of water are added, and the mixture is heated quickly. When it is boiling, 5 ml of the mixed reagents are added and the soln. is kept boiling gently. The time to complete decolorisation (4 to 10 min.) is measured; results can be read off from a calibration graph. SUGAR IND. ABSTR.

1508. The nitrogen content of lean pork. C. R. Marshall (Excel Co. Ltd., Carpenters Road, Stratford, London). *Analyst*, 1955, **80**, 776–778.—Low results were obtained when the meat contents of pork sausages of known composition were calculated from the results of analysis. The method was that of Stubbs *et al.* (*Analyst*, 1919, **44**, 125) with the use of the corrected factor 100/3·6 of Jackson *et al.* (*Brit. Abstr. B*, 1932, 959) to convert meat nitrogen into defatted meat. Sampling error is excluded as a possible explanation and, in order to account for the deficiency, the distribution of N in a headless side of home-killed pork was examined. The average nitrogen contents of the defatted meats

were lower than those obtained by Jackson *et al.* (*loc. cit.*) and accounted for the discrepancies originally observed. Changes in methods of feeding during recent years may possibly account for the differences between the factors found and those of Jackson *et al.* Breed also may have a contributory effect. A. O. JONES

1509. Separation of creatine and creatinine by paper chromatography and the quantitative estimation of total creatinine in food. L. Acker, W. Diemair, D. Pfeil and G. Schiffner (Univ. Inst. Food Chem., Frankfurt, Germany). *Z. anal. Chem.*, 1955, **148** (1), 10–14.—Creatine and creatinine are separated by paper chromatography, a mixture of butanol, acetic acid and water (4:1:5), to whose organic layer 20 per cent. of methanol is added, being used as solvent. On a Whatman No. 1 paper at 27° C, R_F values of 0·42 and 0·55 are given for creatine and creatinine, respectively. The chromatogram is dried at 100° C and the zones are revealed by spraying first with 2 N NaOH and then with a 1·2 per cent. picric acid soln. For the quant. estimation of total creatinine, the creatine is first converted into creatinine by evaporating with HCl for 2 hr. before chromatography. As the colour reaction with NaOH and picric acid is best carried out after dissolving the creatinine from the paper, the zone is located with the help of a control chromatogram. In this instance, the chromatogram is air-dried and not warmed. The zone containing the creatinine is cut out and allowed to stand for 10 min. in a test-tube with 1 ml each of 2 N NaOH and 1·2 per cent. picric acid soln. After the addition of 10 ml of H_2O, the colour is completely extracted by shaking. The soln. is filtered and its extinction is measured photometrically with an S50 filter in a 1-cm cell against a blank prepared from a piece of filter-paper of the same size. The photometer is calibrated with standard soln. containing 5 to 100 μg of creatinine. By this method, amounts of creatinine from 5 to 90 μg have been determined with a mean deviation of $\simeq \pm 1$ per cent. (relative). Details are given for the estimation of total creatinine in meat extracts and in meat-broth pastes and cubes. J. H. WATON

1510. Phospholipids in milk. I. Method for the determination of lecithin, kephalin and sphingomyelin in milk. B. S. Baliga and K. P. Basu (Indian Dairy Res. Inst., Bangalore, India). *Indian J. Dairy Sci.*, 1955, **8** (3), 119–128.—The method of Ranney *et al.* (*J. Biol. Chem.*, 1949, **180**, 307) for the determination of lecithin, kephalin and sphingomyelin in fowl plasma and liver has been adapted to the determination of these fractions in milk. The method is based on the adsorption of the total phospholipids on MgO, selective elution of lecithin and sphingomyelin, followed by selective hydrolysis of the lecithin to acid-soluble compounds of P. The total P in the various fractions is determined colorimetrically by King's method (*Biochem. J.*, 1932, **26**, 847). S. C. JOLLY

1511. An extraction - titration method for the determination of free fatty acids in rancid milk and cream. E. N. Frankel and N. P. Tarassuk (Univ. California, Davis, U.S.A.). *J. Dairy Sci.*, 1955, **38** (7), 751–763.—From a study of the methods available and of the factors affecting the recovery of fatty acids (**I**) from rancid milk and cream it is concluded that no method yet available permits quantitative recovery of all **I**. By the method

described, a 95 to 100 per cent. recovery of high-mol.-wt. **I** and 52 to 58 per cent. of low-mol.-wt. **I** (butyric, caproic and capric) are attained, giving about 90 per cent. of total **I**. Neither high- nor low-mol.-wt. **I** are exclusively hydrolysed from milk fat. *Procedure*—Mix 10·0 ml of milk (or less of cream in proportion to the fat content) with 10 ml of neutralised (phenolphthalein) 95 per cent. ethanol in a 50-ml centrifuge tube. Stopper, shake for 1 min., add 15·0 ml of a mixture (2:3) of ether and light petroleum (boiling range 35° to 60° C), shake for 1 min. and centrifuge for 3 min. at 1500 r.p.m. Mix 5·0 ml of the clear supernatant layer with 15 ml of 95 per cent. ethanol containing 5 drops of 1 per cent. ethanolic phenolphthalein, previously neutralised to a pink colour. Titrate with 0·025 N ethanolic KOH to the original colour and calculate the free **I** as ml of N alkali required per gram of milk fat (determined separately).   W. H. C. SHAW

1512. A note on the thiobarbituric acid test for milk lipid oxidation. S. Patton and G. W. Kurtz (Pennsylvania State Univ., U.S.A.). *J. Dairy Sci.*, 1955, **38** (8), 901.—Absorption curves of the colours given by certain $\alpha\beta$-unsaturated aldehydes in the thiobarbituric acid test (Sidwell *et al.*, *J. Amer. Oil Chem. Soc.*, 1955, **32**, 13) are described in detail and the mechanism of the reaction is discussed.
W. H. C. SHAW

1513. A photometric method for estimating the lipase content of milk. T. L. Forster, C. Jensen and E. Plath (North Dakota Agric. Exp. Sta., Fargo, U.S.A.). *J. Dairy Sci.*, 1955, **38** (7), 764–774.—In the method described, 0·5 ml of raw milk is mixed with borate buffer (pH 8·6) and a substrate containing the butyryl ester of 2-naphthol-6-sulphonic acid (**I**). After incubation for 15 min. at 40° C, enzyme action is stopped and proteins are precipitated with trichloroacetic acid. An aliquot of the filtrate is diluted and the liberated **I** is determined colorimetrically with Folin and Ciocalteu's phenol reagent. The result is expressed as lipase units, for which a definition is proposed. Details are given for preparing the butyryl, caproyl and caprylyl esters of **I**.   W. H. C. SHAW

1514. Antibiotics in fluid milk. H. Welch, W. R. Jester and J. M. Burton (Div. Antibiotics, Food and Drug Admin., Washington, D.C., U.S.A.). *Antibiot. & Chemother.*, 1955, **5** (10), 57)–573.—In a survey of 474 samples of raw and pasteurised milk from 16 areas of the U.S.A., penicillin was found in 11·6 per cent. of the samples in concentrations from 0·003 to 0·08 unit per ml. Authoritative opinions on the importance of such levels are given.
W. H. C. SHAW

1515. A quantitative procedure for the determination of an inhibitory substance (penicillin) in milk. L. R. Mattick, E. O. Anderson and H. L. Wildasin (Storrs Agric. Exp. Sta., Connecticut, U.S.A.). *J. Dairy Sci.*, 1955, **38** (8), 829–834.—The method described is based on the inhibition by penicillin of the formation of nitrite from nitrate by an actively growing culture of *Micrococcus pyogenes* var. *aureus*. The decreased nitrite production, as compared with a control, is determined colorimetrically by diazotisation of sulphanilic acid and coupling with 1-naphthylamine hydrochloride. The method is suitable for concentrations up to 1 unit per ml, above which the precision attainable decreases. A linear relationship is obtained between the

logarithms of the penicillin concentration and the standardised colorimeter reading.
W. H. C. SHAW

1516. Identification of traces of *i*sovaleric acid in butter adulterated with hydrogenated dolphin oil. G. D'Arrigo (Centro Sperimentale l'Ind. Olii, Grassi, Saponi, Catania, Sicily). *Olii Min.*, 1955, **32** (7), 147–148.—In an answer to criticisms it is claimed that the author's method (*Anal. Abstr.*, 1955, **2**, 1667) does not suffer from losses during the concentration of potassium salts, and the chromatogram spots are not diffuse.   T. P. McLAUGHLIN

1517. Determination of fructosans in artichoke juice by means of paper chromatography. I. R. Rominskiĭ, A. S. Sushkova and P. V. Golovin. *Ukr. Khim. Zh.*, 1955, **21** (3), 394–399.—The juice is treated with milk of lime, to 1 per cent. of CaO, and CO_2 is passed through the filtrate until a pH of 9 is reached. The solution is then passed successively through a cationite and an anionite column, concentrated *in vacuo* to a content of 30 per cent. of dry matter, and kept at 0° C for 4 days, to ppt. inulin. The filtrate is chromatographed, with butanol - pyridine - water (3:2:1) as solvent, the chromatograph is developed with 1-naphthol, sections of duplicate strips corresponding to the location of spots given by fructose, sucrose and ketose are extracted with water, and their sugar content is determined colorimetrically, with anthrone reagent. The tuber-juice saccharides contained sucrose 4, ketose 8 and an unidentified tetrasaccharide 9·5 per cent.   R. TRUSCOE

1518. Determination of the degree of protein solution of malt by precipitation with tungstophosphoric acid in Congress worts. M. Lindemann (Cenovis Werke, Munich). *Brauwissenschaft*, 1955, **8** (12), 285–289.—The following method for determining the nitrogen pptd. by tungstophosphoric acid is reported and discussed. To a laboratory-mashed wort (100 ml) at room temp. add 10 per cent. H_2SO_4 (5 ml) and 10 per cent. tungstophosphoric acid (5 ml), allow to settle and filter off the ppt. Wash several times with 0·5 per cent. H_2SO_4. The nitrogen is then determined by the Kjeldahl method. The ratio of the total soluble nitrogen to the nitrogen pptd. by tungstophosphoric acid is called the "P.W.V." Experiments show that this ratio is lower in worts from a malt having a high or normal percentage content of soluble protein than from a malt in which this is low. The possibility of using "P.W.V." to assess malt suitability is discussed.   G. H. BAKER

1519. Determination of carbon dioxide in canned and bottled beer. C. J. Barker and T. L. Parkinson (Metal Box Co. Ltd., Acton, London). *J. Inst. Brewing*, 1955, **61** (6), 512–518.—When the beer bottles or cans (cooled to 0° C) are opened before the beer is mixed with alkali, small but significant losses of CO_2 are found to occur when the ratio of CO_2 to beer (v/v at 0° C) exceeds 2·5. In the present method, this loss is obviated by the use of a piercing tool which is connected by transparent tubing with a large evacuated round flask. A conventional piercer can be used for bottles and cone-topped cans; a specially designed tool is used for dealing with flat-topped cans. The beer and the headspace gas are thus drawn into the flask through a glass tube, which is sealed into the stopper of the flask, to a point near the bottom of the flask, which has previously been charged with 10 ml of aq. 40 per

cent. NaOH.   Any CO_2 which may escape absorption in the flask is trapped in two absorption bottles containing N KOH soln., which are placed between the flask and the vacuum-pump.   The CO_2 (combined) in the alkaline beer is determined by a simple adaptation of Fuller's gasometric method (cf. *Analyst*, 1945, **70**, 87), and the CO_2 absorbed by the N KOH soln. is determined titrimetrically, first with the use of a mixture of thymolphthalein and phenolphthalein, then with methyl orange as indicators.   The results obtained are in good agreement with those obtained by the A.O.A.C. chemical method.   P. S. ARUP

1520. Comparative studies of methods of hop analysis. II. Estimation of humulone and other resin constituents.   L. R. Bishop (Stag Brewery, Pimlico, London).   *J. Inst. Brewing*, 1955, **61** (6), 472–487.—This report, submitted for the E.B.C. Analysis Committee, includes a review of the chemistry and relative bittering values of the hop-resin constituents, and the results of collaborative studies of the Ford and Tait (Gough modification), Wöllmer, Walker and Hastings, and the Govaert and Verzele methods, with special attention to the determination of the humulones.   Good general agreement is shown between the results of the four different methods, but the methods are subject to the following important sources of error.   (a) In all the methods there is a danger of the destruction of soft resins by oxidation and sunlight.   (b) With the first three methods, high (or low) results are obtained by the use of impure methanol, low results are obtained with old hops, and incorrect results may be obtained owing to the difficulty of determining the lead-pptn. end-point.   (c) With the Ford and Tait method, high results for humulones may be obtained owing to the co-pptn. of waxes. Suitable precautions are given for the elimination or minimising of these errors, and improved methods for the calculation of the results are recommended.   P. S. ARUP

1521. Determination of bitter-tasting conversion products of hops in wort and beer.   A. B. Moltke and M. Meilgaard (Carlsberg Brewery Res. Lab., Copenhagen, Denmark).   *Brauwelt*, 1955, **B95** (75), 1265–1270.—The countercurrent-extraction method of Rigby and Bethune (cf. *Proc. Amer. Soc. Brewing Chem.*, 1952, 98) for the determination of *iso*humulone, *iso*cohumulone and *iso*adhumulone in wort or beer is examined, and minor modifications are recommended.   A rapid simplified method proposed by Rigby (private communication) and improved by the author gives results that agree well (within 5 per cent.) with the results obtained by the former method, and that show reproducibility within 2 per cent.   This method gives total "*iso*humulone" contents, based on a mean spectrophotometric extinction value of 287 for the three *iso*humulones; it is suitable for routine work in the determination of the degree of utilisation of the hop bitters in brewing, and the stability of the bitters in beer; it is more reliable with respect to the bitters from fresh, than from those from old, hops.   *Procedure*—The whole operation, including the preliminary elimination of CO_2 from the beer, must be carried out at $20° \pm 0.5°$ C.   To the CO_2-free sample (20 ml) contained in a glass-stoppered flask, add 1 ml (± 0.05 ml) of 6 N HCl and 20 ml of *iso*octane, and shake for 5 min.   Centrifuge the mixture during 10 to 15 min. at 3000 r.p.m., and determine the spectrophotometric extinction value at 275 mμ in the *iso*octane phase.   The *iso*humulone

content, in mg per litre, is given by the formula $28.6 \ E_{275} - 5.9$, where E_{275} is the extinction value determined in a 1-cm optical cell.   In this formula, the values obtained by the rapid method are converted into the values to be expected with the use of the original countercurrent-extraction method. Procedures are described for the preparation of an organoleptic "bitter scale" consisting of a series of beers of known *iso*humulone contents.

P. S. ARUP

1522. Separation of permitted coal-tar food colours by paper chromatography. I.   S. N. Mitra and R. K. Chatterji (West Bengal Public Health Lab., Calcutta, India).   *J. Inst. Chem., India*, 1955, **27** (3), 169–176.—The coal-tar colours (water-soluble acid dyes, erythrosine, orange I, tartrazine, indigotin and amaranth) whose use in foodstuffs is permitted have been separated and identified both in aqueous solution and in one article of food (fruit squash) by paper chromatography.   Two techniques were used—(a) vertical-column paper chromatography (ascending type) and (b) circular paper disc (horizontal type).   The most suitable solvents were 5 per cent. NaCl solution and 1 to 0·25 N HCl.   The order of separation (in decreasing height) was tartrazine, indigotin, amaranth, orange I and erythrosine.   I. JONES

1523. Method of differentiation between refined and non-refined oils and fats.   S. H. Bertram. *Rev. Ferment. Ind. Aliment.*, 1955, **10**, 165–166.—A method for distinguishing between refined and crude oils and fats, based on the marked diminution in electrical conductivity as a result of refining, is outlined.   A sample of $\simeq 150$ ml is filtered and dried under vacuum at 125° C; 100 ml are placed in a cupro-nickel or stainless-steel vessel and its specific resistance is determined, with a high-resistance electronic voltmeter and a high-tension current.   At 100° C, the specific resistance of crude oils and fats varies from 140 to 1250×10^{12} ohm per cu. cm, as compared with 3 to 15×10^{12} ohm per cu. cm for the corresponding refined products.   S.C.I. ABSTR.

1524. Polarographic estimation of vitamin A. Preliminary communication.   W. Keller and F. Weiss (Pharm. Inst., Humboldt Univ., Berlin, Germany).   *Z. anal. Chem.*, 1955, **148** (1), 26–29.— Vitamin A is estimated rapidly and accurately by a polarographic method.   The solvent used is anhyd. methanol, and the supporting electrolyte consists of a 1 per cent. soln. of NH_4NO_3 in methanol.   The vitamin A is first iodinated with a 0·4 per cent. soln. of I in methanol, and then estimated with a Heyrovský micro-polarograph.

J. H. WATON

1525. A multiple regression study of the Carr - Price reaction for vitamin A in the presence of carotene.   J. E. Rousseau, H. D. Eaton, G. Beall and H. L. Lucas (Storrs Agric. Exp. Sta., Connecticut, U.S.A.).   *J. Dairy Sci.*, 1955, **38** (8), 902–903.—With pure solutions, carotene has been found to contribute to the colour given in the Carr - Price reaction in a linear and additive manner.   A method is described in which multiple regression analysis may be used to estimate the amount of interference that carotenoids may cause when the Carr - Price reaction is applied to biological materials.   W. H. C. SHAW

1526. New colour reaction for vitamin D. W. I. Lyness and F. W. Quackenbush (Purdue Univ., Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1978–1980.—Vitamins D_2 and D_3 interact with an iodine - dichloroethane reagent to produce a yellow colour with absorption max. at 450 mμ. The intensity of the colour is enhanced by the presence of mercuric p-chlorobenzoate and certain other compounds. The colour is specific for the vitamins D. No colour was given by various sterols, but vitamin A produced a weak violet colour which showed slight absorption at 450 mμ. This reagent is more sensitive and specific than the glycerol dichlorohydrin reagent, but is less sensitive than the $SbCl_3$ reagent. G. P. COOK

1527. Determination of thiamine in vitamin concentrates containing Creta Praeparata. H. N. Ridyard (Cereals Res. Sta., St Albans, Herts., England). *Analyst*, 1955, **80**, 834–837.—An investigation of the effect of variations in the method of extraction of thiamine from vitamin concentrates containing Creta Praeparata showed that the use of much strong acid is necessary and that, owing to adsorption of thiamine on insol. residues, vigorous shaking of the liquid before determination is essential. The best results were obtained by two procedures—(*a*) the mixture (5 g) in a 500-ml flask is treated with 75 ml of conc. HCl added in $\simeq 3$ portions with vigorous shaking and (*b*) 5 g of the mixture are added very gradually to 75 ml of conc. HCl in a 2-litre beaker, with constant shaking. The extract from either method is diluted to 500 ml and mixed thoroughly, and 30-ml aliquots are diluted to 200 ml, the concn. of HCl being then $0\cdot24 N$. Thiamine is determined by the thiochrome method (Ridyard, *Brit. Abstr. C*, 1949, 298). Certain necessary precautions in the blank determination are described. A. O. JONES

1528. Polarography of thiamine. II. Polarographic determination of thiamine in presence of ascorbic acid. A. M. Shkodin and G. P. Tikhomirova (Ukr. Sci. Res. Inst. Food Industry, Kharkov, Ukrain. SSR). *Ukr. Khim. Zh.*, 1955, **21** (2), 265–268.—In $0\cdot1 N$ KCl the $E_{\frac{1}{2}}$ of thiamine is $-1\cdot25$, and of ascorbic acid $-1\cdot63$ V. When both substances are present together only one wave is observed, the $E_{\frac{1}{2}}$ of which is very close to that of thiamine, but the height of which rises linearly with ascorbic acid concn. This effect is ascribed to catalysis by thiamine of liberation of $H^{\cdot}$ from ascorbic acid, and is abolished at pH 7. Thiamine in yeast extracts is determined by adjusting the pH of the extracts to pH 7, and comparing the height of the polarographic waves before and after addition of standard thiamine solutions. R. TRUSCOE

1529. The influence of thiamine on the microbiological assay for vitamin B12 with *Escherichia coli* 113-3. J. M. McLaughlan, C. G. Rogers and J. A. Campbell (Food & Drug Lab., Dept. of Nat. Hlth & Welfare, Ottawa, Canada). *J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** (10), 594–598.—The presence of thiamine in multi-vitamin preparations is shown to be responsible for the low results of tube assays, with *E. coli* 113–3 as a test organism, on the Davis and Mingioli medium. Both stationary and shaken assays were incubated at 31° C for 16 hr., and the resulting turbidities were determined at 540 mμ. These preparations, when extracted with a 1 per cent. $Na_2S_2O_5$ soln., give results that are comparable with those obtained in the U.S.P. method, thereby eliminating the cyanide treatment;

their use is suggested for the estimation of vitamin-B_{12} activity in the absence of interfering compounds, *e.g.*, dried yeast or the pseudo forms of vitamin B_{12}. G. R. WHALLEY

1530. Countercurrent analysis of vitamin B12. W. J. Mader and R. G. Johl (Merck & Co., Inc., Chemical Div., Rahway, N.J., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** (9), 577–579.—The method described is specific for determining the purity or cyanocobalamin content of cryst. vitamin B_{12}, oral-grade solids and simple solutions. The presence or absence of pseudocobalamin and other non-cobalamin fractions may also be determined. Results agree well with those obtained by the radioactive-tracer method. To a sample equiv. to $\simeq 50 \mu g$ of vitamin are added 50 ml of H_2O, 5 ml of KCN soln. (10 per cent.) and 5 ml of $NaNO_2$ soln. (2 per cent.) and the pH of the resulting solution is adjusted to 4 with $6 N$ acetic acid. The solution is boiled, then cooled, and 1 ml of formaldehyde solution (37 per cent.) is added before filtration. Half of the combined filtrate and washings is extracted with cresol - CCl_4 (1 : 1) and the extract is washed first with $5 N$ H_2SO_4 and then with $NaHCO_3$ (2 per cent.) - KCN (0·4 per cent.) solution. To the washed extract are added 20 ml of $CHCl_3$, 5 ml of butanol and 5 ml of H_2O. The aqueous layer is separated centrifugally and the extraction is repeated with two further 5-ml portions of H_2O; the volume of the extract is made up to 25 ml. Aliquots of this solution are used for the countercurrent distribution in 8 tubes; the solvent system employed is benzyl alcohol shaken with an equal vol. of water till both phases are mutually saturated. The B_{12} content of the phases is determined microbiologically, spectrophotometrically or colorimetrically. N. M. WALLER

1531. A new titrimetric method for the determination of ascorbic acid. M. Z. Barakat, S. K. Shehab and M. M. El-Sadr (Ibrahim Pasha El-Kebir Univ., Cairo). *Analyst*, 1955, **80**, 828–833.—The method is based on the rapid quant. reduction of the orange-coloured sodium 1 : 2-naphthaquinone-4-sulphonate to the colourless corresponding quinol. A metaphosphoric acid - acetic acid soln. is added to the prepared sample soln. which is then diluted so that 100 ml contain 0·5 to 2·0 mg of ascorbic acid. A known vol. of the standard soln. of the reagent (0·26 g, *i.e.*, 1 millimole per 100 ml) is then titrated with the sample soln. Examples are given of the application of the method to pharmaceutical products and to citrus juices and the results obtained are compared with those obtained by the 2 : 6-dichlorophenolindophenol method. The main advantages of the new method are the stability of the reagent soln. and the absence of interference by iron salts and some other compounds affecting the older method. Interference occurs with alkali sulphites, sulphides and thiosulphates, and with thiourea. The experimental error is ± 2 per cent. A. O. JONES

1532. The bound form of ascorbic acid. IX. Fluorimetric determination of ascorbigen. V. Šícho and E. Bradáčová (Dept. Biol. Sci., Chem.-Tech. High School, Prague, Czechoslovakia). *Českosl. Farmac.*, 1955, **4** (9), 451–454.—On hydrolysis of ascorbigen (**I**) with mineral acid in the presence of formaldehyde, an unknown compound is formed which fluoresces yellow in u.v. light. For this reaction $2 N$ HCl containing between 5 and 10 per cent. of formaldehyde is most suitable. The

intensity of fluorescence is related linearly to the concn. of **I** between 0·15 and 1 μg per ml of soln., and is independent of the pH between 1 and 3, thereafter decreasing rapidly. Use was made of this to determine **I** in plant juices in the presence of other fluorescing substances not affected by alkali. The fluorescence can also be reduced by intense u.v. irradiation for 45 min. Some indole derivatives, such as indol-3-ylacetic and indol-3-yl-propionic acids, tryptophan, etc., also give fluorescing products with formaldehyde. When these are present, paper chromatography is used to separate **I**. A mixture of butyl acetate and water is used as developer, and water or methanol as eluent. 　　　　　　　　A. O. Jakubovic

1533. Determination of vitamin E (total natural tocopherols) in vegetable oils. B. G. Savinov, G. M. Lushchevskaya and L. A. Musiĺko. *Ukr. Khim. Zh.*, 1954, **20** (5), 573–577.—A solution of 1 g of the oil and 0·1 g of pyrogallol in 4 ml of methanol is heated under reflux in a stream of inert gas, and 1 ml of 60 per cent. aq. KOH is added. Boiling is continued for 5 to 7 min., and the mixture is cooled, diluted with 40 ml of H_2O, and extracted with ether (3 × 15 ml). The extract is washed with H_2O and 5 per cent. aq. KOH, and with H_2O (the washings are tested for pyrogallol and alkali). It is then dried by filtration through Na_2SO_4, the ether is distilled off, and the residue is dissolved in 5 ml of benzene. The benzene solution is further purified by filtration through diatomite in a 15-cm × 1-cm column (diatomite layer 1 cm thick, with a little Na_2SO_4 above). A filter-pump is used to draw the solution through the column, which is washed down with 25 ml of pure benzene (testing for complete extraction of tocopherols by $FeCl_3$ and 2:2′-dipyridyl). The benzene is distilled off *in vacuo*. The residue is dissolved in abs. ethanol and the solution is made up to 25 ml. A measured quantity of this solution (≡ 0·15 to 0·35 mg of tocopherols) is treated with 1 ml of 0·2 per cent. $FeCl_3$ soln. and 1 ml of 0·5 per cent. 2:2′-dipyridyl (both in abs. ethanol). The colour is measured in a photometer (green filter) and the tocopherol estimated from a calibration curve. Results are more reliable than those obtained by the HNO_3 method, which is affected by the presence of tocopherolquinones. 　　　　　　　　F. W. Kirkbride

See also Abstracts 1297, 1412, 1553, 1578.

Sanitation

1534. Standard methods for the examination of water, sewage and industrial wastes. American Public Health Association Inc. (New York, U.S.A.). 1955, 542 pp.—In the tenth edition of Standard Methods, prepared jointly by the American Public Health Association, the American Water Works Association and the Federation of Sewage and Industrial Wastes Association, the introductory chapter on sampling, general analytical technique, and expression and interpretation of results has been extensively revised. Spectrography, polarography, electro-titrators and other newer analytical apparatus are dealt with. In the chapter on bacteriology, a tentative procedure for the use of membrane filters in determining coliform bacteria is included. In a new section on the biological examination of water, sewage sludge and bottom deposits, methods and equipment for sampling

plankton and bottom fauna are described, and illustrations are given of the commonest plankton and bottom organisms.
　　　　　　　　Water Pollution Abstr.

1535. Determination of traces of copper in water. M. Kovařík and V. Vinš (Inst. for Anal. Chem., School of Mining, Ostrava, Czechoslovakia). *Z. anal. Chem.*, 1955, **147** (6), 401–403.—A method is given for the photometric estimation of traces of Cu in water, including mineral water. When the sample is shaken with a soln. of Pb diethyldithiocarbamate in $CHCl_3$, Cu is extracted together with Ag and Hg, which do not interfere. *Procedure*—To a 500-ml sample of the water are added 10 ml of a 10 per cent. soln. of K Na tartrate and 10 ml of $2 N$ NH_4Cl soln., and then the soln. is made weakly alkaline with aq. NH_3. The soln. is shaken with 10 ml of a $CHCl_3$ soln. of Pb diethyldithiocarbamate and the yellow to brown layer of Cu diethyldithiocarbamate is separated. The extinction of the copper compound is measured at 500 mμ in a 1-cm cell, an S50 filter being used. The method enables amounts of Cu from 0·02 μg per ml to be determined with a relative error of ≃ ±1·5 per cent. The Pb diethyldithiocarbamate reagent is prepared as follows. Lead acetate (0·1 g) is dissolved in water and 5 ml of a 10 per cent. K Na tartrate soln. are added. The soln. is made alkaline with $2 N$ KOH soln., and 5 ml of N KCN soln. are introduced to complex traces of Cu and Fe. Sodium diethyldithiocarbamate (0·12 g) in water is added, and the pptd. lead salt is extracted in 250 ml of $CHCl_3$. The organic layer is removed, shaken with water, re-separated, filtered and made up to 1 litre. 　　　　　　　　J. H. Waton

1536. Determination of B.O.D. by a re-aeration technique. H. L. Elmore (Stream Pollution Control Lab., Chattanooga, Tenn., U.S.A.). *Sewage Ind. Wastes*, 1955, **27** (9), 993–1002.—The technique described is primarily designed to determine the B.O.D. of samples derived from streams and reservoirs and consists in incubating several sealed bottles of a sample and a larger unsealed bottle of the same sample. The dissolved O is measured by the Winkler method, initially and at various intervals. When total depletion of the O is approached, another set of sealed bottles is prepared from the unsealed bottle and the procedure is continued through any time interval desired. Re-aeration is carried out by adjusting the sample temp. to ≃ 23° to 25° C, removing supersaturated O by vacuum, then aerating for 15 min. with a diffusion stone to assure a stable dissolved-oxygen content. A low rate of stirring is applied to ensure even distribution of suspended solids and the necessary number of bottles is filled by siphoning. The samples remaining are mixed and re-aerated by the same procedure as soon as the dissolved O in a sample is found to approach 1 p.p.m. A device, comprising a magnetic stirrer, a thermostatically controlled heater and various tubes and valves to control the flow of air and sample, is described. 　　　　　　　　S.C.I. Abstr.

1537. Procedures for analysing metal-finishing wastes. Ohio River Valley Water Sanitation Commission. Report, 1954, 102 pp.—The precautions that should be taken in collecting samples for analysis are described and procedures are given for determining 5 to 50 p.p.m. of a substance in the presence of 100 to 5000 p.p.m. of each of about 23 elements. The methods have proved satisfactory

in the field. The tests described include those for cyanide, cyanate, Cd, Cr, Cu, Fe, Pb, Mn, Ni and Zn and revised procedures for the determination of ammonia, chloride, Cl, nitrate and nitrite nitrogen, orthophosphate, sulphate, and dichromate oxygen demand (all designed specifically to avoid interference by ions normally present in metal-finishing wastes). To make a complete analysis of plating-waste waters, pH value, and concentrations of total, suspended and dissolved solids and solids that settle are also necessary and these methods are reproduced from the American Public Health Association's publication of standard methods.

WATER POLLUTION ABSTR.

1538. Thiourea derivatives as rodenticides and their identification in cases of [domestic] animal poisoning. A. Schöberl and G. Wiehler (Chem. Inst. Tierärz. Hochsch., Hanover, Germany). *Angew. Chem.*, 1955, **67** (16), 417–420.—A process for the identification and colorimetric determination of "Antu" (1-naphthylthiourea) (**I**) and "Muritan" preparations [4-chlorophenyldiazothiourea ("Promurit") (**II**) and 3 : 4-dichlorophenyldiazothiourea ("Chlorpromurit") (**III**)] has been developed. The active substances from stomach contents, urine, or feeding samples (200 g) are extracted with methanol (2 × 200 ml). The clear (centrifuged) extracts are evaporated, the semi-solid residue is hydrolysed with 25 ml of 60 per cent. H_2SO_4 (by refluxing at 140° C for 1 hr.), made alkaline (by gradual addition of $\simeq 50$ per cent. NaOH soln.) and steam-distilled to obtain the liberated aromatic amines. For the determination of **I**, 1 to 20 ml of the aq. 1-naphthylamine are treated with 20 to 25 ml of methanol and converted into the red azo dye by adding 5 to 6 drops of diazotised sulphanilic acid (preparation described). The solution is then diluted to 50 ml with methanol, and its extinction is measured in a Pulfrich photometer and compared with that of standard solutions. For the determination of the "Muritan" preparations, the steam-distillate (obtained as above) is acidified with 2 ml of 2 N HCl, transferred to an ice-bath and treated with 1 ml of 0·1 per cent. NaNO$_2$. After 3 min., the cooled solution is treated with 1 ml of 0·5 per cent. ammonium sulphamate and after another 2 min. with 1 ml of 0·1 per cent. N-(1-naphthyl)-ethylenediamine hydrochloride. The mixture is diluted to 50 ml, with H_2O for **II**, with methanol for **III**. The isolation of *p*-chloroaniline and of 3 : 4-dichloroaniline by the decomposition of **II** and of **III**, respectively, is described. S.C.I. ABSTR.

See also Abstracts 1298, 1392, 1426, 1583, 1591.

Agriculture and Plant Biochemistry

1539. The determination of 3 : 5-dinitro-o-cresol in the presence of β-carotene in biological tissues. M. L. Fenwick and V. H. Parker (Pest Control Ltd., Bourn, Cambridge). *Analyst*, 1955, **80**, 774–776.—The method described for the determination of 3 : 5-dinitro-*o*-cresol (**I**) in the presence of carotene depends on the fact that whereas the Na salt of **I** is bright yellow and the free acid almost colourless in ethyl methyl ketone, the extinction of β-carotene at 430 mμ is the same in acid and alkaline solution. Two procedures are described. In the first, devised for application to cows' blood, 1 ml of the blood is dispersed with 5 ml of ethyl methyl ketone and is shaken with a mixture of NaCl and Na_2CO_3. The extinction of the filtered supernatant liquid is determined at 430 mμ. The liquid is then acidified

and centrifuged and the extinction is again determined, the difference being equivalent to the concn. of **I**. This is ascertained from a calibration graph. The second method was devised to determine **I** on locusts. The locust is homogenised with chloroform and trichloroacetic acid, the liquid is centrifuged and **I** is extracted from the chloroform layer with Na_2CO_3 soln., which is then extracted with ethyl methyl ketone in the presence of NaCl and the extinction of the ketone extract is determined at 430 mμ. Both methods are applicable to other similar problems. A. O. JONES

1540. Labile chlorine method for estimation of dieldrin. S. K. Majumder and S. V. Pingale (Central Food Tech. Res. Inst., Mysore, India). *Chem. & Ind.*, 1955, (52), 1739.—Tests described with ethanolamine show that 2 to 3 mol. of chlorine become labile in dieldrin (**I**) under aerated and non-aerated conditions of dehydrochlorination. For complete dehydrochlorination of labile chlorine, **I** has to be heated at 140° C for 12 to 16 hr. Since DDT, BHC, Chlordane and Toxaphene are dehydrochlorinated by heating at 100° C for 1 hr., but **I** is not, **I** can be estimated in mixtures with these chemicals by using ethanolamine. The technique can be used for estimating technical **I**, since the chloro impurities in it react with ethanolamine at 100° C. O. M. WHITTON

1541. Colorimetric determination of ethyl 4 : 4′-dichlorobenzilate (Chorobenzilate) as spray residue. H. J. Harris (Geigy Agric. Chemicals, Bayonne, N.J., U.S.A.). *J. Agric. Food Chem.*, 1955, **3** (11), 939–941.—A modification of the Schechter-Haller procedure is described for the determination of residual Chlorobenzilate on such crops as apples or pears. The compound is nitrated and treated with Na methoxide; a red complex is formed which is measured spectrophotometrically at 538 mμ. If DDT is present in the spray the DDT is dechlorinated with alcoholic KOH and extracted with light petroleum. The Chlorobenzilate is saponified to the potassium salt of 4 : 4′-dichlorobenzilic acid, then converted into the acid. After nitration the same coloured compound is formed with Na methoxide as given by the ester, with max. absorption at 538 mμ. S.C.I. ABSTR.

1542. Determination of Lindane (gamma-hexachlorocyclohexane) in mushrooms. I. Hornstein (Agric. Res. Serv., U.S. Dept. Agric., Beltsville, Md., U.S.A.). *J. Agric. Food Chem.*, 1955, **3** (10), 848–849.—The mushrooms (100 g) are washed, cut into small pieces and refluxed for 3 to 4 hr. with dichloromethane (200 ml). After standing overnight, the extract is decanted through a filter-paper into a separating funnel, the small amount of water is separated and the vol. of dichloromethane is reduced to $\simeq 50$ ml on a water bath. The extract is then sulphonated with three separate 10-ml portions of 30 per cent. fuming H_2SO_4; 25 ml of cold water are then cautiously added to the dichloromethane, this washing process being repeated with two further 25-ml portions of water. The dichloromethane is evaporated to a vol. of 1 to 2 ml and 120 ml of glacial acetic acid are added; 20 ml of the acid are distilled by heating to between 130° and 140° C in an oil bath to remove the last traces of volatile solvent, and the glacial acetic acid soln. is analysed by the method of Schechter and Hornstein (*Anal. Chem.*, 1952, **24**, 544). S.C.I. ABSTR.

See also Abstracts 1341, 1517, 1551.

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

General

1543. Apparatus for the measurement of extremely small weight, volume and density changes. W. K. Haller and G. L. Calcamuggio (Inst. Silicate Res., Univ. Toledo, Ohio, U.S.A.). *Rev. Sci. Instrum.*, 1955, **26** (11), 1064–1068.—A pressure-controlled hydraulic balance for the measurement of small density changes is described. The movement of a calibrated compressible all-glass float carrying the sample is observed while the pressure on the float is adjusted until movement ceases. The float is a sealed Pyrex-glass bulb having a flat portion which acts as an elastic membrane. The sample is maintained in a nickel cradle suspended from the float.
G. SKIRROW

1544. A simple storage burette for air-sensitive solutions. A. G. Hamlin (Shirley Inst., Didsbury, Manchester, England). *Analyst*, 1955, **80**, 843–845. —A simple storage burette is described for use with air-sensitive reducing soln., *e.g.*, chromous or titanous soln. The reservoir is a vacuum flask closed by means of a rubber stopper carrying, through separate holes, a 2-mm-bore capillary tube reaching to the bottom of the flask and bent twice at right angles and furnished with a tap, and a burette without a tap, the stem of which reaches only to the inner surface of the stopper. The soln., which occupies about two-thirds of the flask, is overlaid with an inert liquid which fills the remaining space and rises into the burette. As the reagent is driven from the flask through the capillary tube by the head in the burette during a titration, the level of the inert liquid sinks in the burette and readings are taken in the usual way. "White spirit" is recommended as the inert liquid because of its negligible drainage error. The apparatus is particularly useful when small amounts of reducing agents are required at infrequent intervals.   A. O. JONES

1545. Rapid and precise measurement of moisture in biological materials. R. J. Heckly (Univ. California, Berkeley, U.S.A.). *Science*, 1955, **122**, 760–761.—An apparatus is described by means of which water can be removed from biological samples and determined by manometric measurement of the water vapour.
H. F. W. KIRKPATRICK

1546. Simple countercurrent distribution apparatus. A. Pinsky and S. Raymond (Agric. Res. Station, Rehovot, Israel). *Anal. Chem.*, 1955, **27** (12), 2019–2020.—An apparatus for the analysis and purification of complex mixtures by a countercurrent technique is described; it has certain advantages in applications where emulsions are a source of difficulty. The operation consists briefly in decanting from one series of tubes to the other and then shifting a detachable frame so as to decant back into the succeeding tube of the first series.
G. P. COOK

1547. Ultrasonic gas analyser. M. Kniazuk and F. R. Prediger (Merck Inst. Therap. Res., Rahway, N.J., U.S.A.). *Instrum. and Automation*, 1955, **28** (11), 1916–1917.—A method is described for the measurement of basal metabolic rates in which the oxygen concentration changes by approximately 0·01 per cent. The gas flows through a metal tube 8 mm in diam. and 100 cm long and the phase change produced by the change in the velocity of sound waves (150·1 kc.) along the tube is measured. The electronic circuits of the ultrasonic analyser are described.
G. SKIRROW

1548. Apparatus for determining small concentrations of oxygen in gases. Yu. V. Sharvin, V. P. Andrianov and E. A. Sharova (S. I. Vavilov Inst. Phys. Problems, Acad. Sci. USSR). *Zavod. Lab.*, 1955, **21** (7), 853–855.—A scheme for the determination of small concentrations of oxygen in hydrogen, 1×10^{-9} parts by vol., is described. The oxygen is adsorbed on silica gel in liquid nitrogen. Desorption gives a gas 1000 times as rich in oxygen as the original gas. The amount is determined colorimetrically, with an ammoniacal copper solution.
G. S. SMITH

1549. Distillation method for determination of small amounts of impurities in gases. V. G. Fastovskiĭ, A. E. Rovinskiĭ and A. A. Vlasova. *Zavod. Lab.*, 1955, **21** (10), 1158–1159.—An apparatus involving condensation and evaporation of gases is described; contents are found from pressure readings. It is suitable for determining the purity of krypton.
G. S. SMITH

1550. A new type of ultrafilter. J. L. Gardon and S. G. Mason (Industrial Cellulose Research, Ltd., Hawkesbury, Ontario, Canada). *Canad. J. Chem.*, 1955, **33** (10), 1625–1629.—The construction and operation of the ultrafiltration unit are illustrated and described. It consists of slightly modified osmometer cells and, by changing their number, the rate of ultrafiltration can be readily varied. The unit has been used for the fractionation of ligninsulphonates. Since the membrane area is large, the unit may be used at relatively low pressure differentials by means of water aspirators. It is fully automatic, simple to construct, leakproof, and allows thorough stirring of the liquid.
O. M. WHITTON

1551. Micro-extraction for paper chromatography. M. H. Zimmermann (Harvard Univ., Petersham, Mass., U.S.A.). *Science*, 1955, **122**, 766.—An apparatus designed for the extraction of the very small amounts of plant tissue needed for paper chromatography is described. A 5-ml flask is fitted with a stoppered horizontal side-arm having a shallow bulb and carrying a reflux condenser just beyond the bulb. The tissue is placed in the bulb and solvent in the flask. When the solvent is boiled the vapour condenses, collects in the bulb and overflows back into the flask to give a continuous extraction.   H. F. W. KIRKPATRICK

1552. Elution of coloured spots from paper chromatograms. H. Streuli. *Mitt. Lebensmitt. Hyg., Bern*, 1955, **46** (4), 340.—In order to elute a coloured substance in the smallest volume possible, it was first brought to the edge of the chromatogram with a suitable solvent. A thin strip containing the substance was cut off and one end fixed in the stem of a funnel. The elution was completed by allowing the solvent to descend the strip in a dropwise manner.   W. H. PARR

1553. A convenient all-glass closed chamber for paper partition chromatography. R. N. Chakravarti and B. Dasgupta (School Tropical Med., Calcutta, India). *J. Inst. Chem., India*, 1955, **27** (3), 177–182.—The system described (Petri dish and bell

jar) is suitable for the paper partition chromatography (ascending type) of sugars obtained by the hydrolysis (HCl) of the saponins isolated from yams of Indian *Dioscorea* plants. Two-dimensional ascending chromatography in an undisturbed saturated atmosphere can be carried out and as many as 15 different spots can be chromatographed simultaneously by using 3 sheets of filter-paper as coaxial cylinders. A spreading technique for the colour reagent is improved by the use of a filter-paper roller. I. JONES

1554. The bar viscometer. D. Tollenaar and M. C. Bisschop (Res. Inst. T.N.O. for Printing and Allied Ind., Amsterdam, Netherlands). *J. Colloid Sci.*, 1955, **10** (2), 151–155.—A simply constructed bar viscometer consists of an accurately machined and polished cylindrical bar, 38·00 mm long and 19·988 mm in diameter, suspended in a holder which is mounted on a stand. When the bar is released it can be balanced by counter-weights. The lower end of the bar projects through a ring, height 20·0 mm and diameter 20·048 mm, fixed into the holder. The liquid whose viscosity is to be measured is put between the bar and the ring. The free end of the bar is loaded and falls through the ring. During the fall it is balanced by a counter-weight and the internal friction of the liquid. The ring can be replaced by rings of slightly larger diameter. Shearing stresses of 10^6 dynes per sq. cm can be reached for highly viscous oils (*e.g.*, 1000 poises). In general the instrument is not suitable for measuring shearing stresses lower than 10^4 dynes per sq. cm. C. A. SLATER

1555. A cone-and-plate viscometer. H. Markovitz, L. J. Elyash, F. J. Padden, jun., and T. W. De Witt (Mellon Inst., Pittsburgh, Pa., U.S.A.). *J. Colloid Sci.*, 1955, **10** (2), 165–175.—A weight-driven cone-and-plate viscometer consists of a cone accurately positioned when the conical surfaces of its integral shaft are held against the bearing surfaces of the spindle in the headstock of a mounted watchmaker's lathe. A known torque is applied to the flat plate by hanging weights on a string, which is led over a pulley. A galvanometer mirror is used to follow the motion of the plate and it is possible to measure a range of speeds from 10^{-6} to 10 r.p.s. The instrument is filled by placing the material on the plate and raising it to the correct position. Liquids with viscosities from 1 to 50,000 poises have been investigated, and rates of shear from 0·0002 to 9000 sec.$^{-1}$ have been achieved. With one filling of the viscometer, a 1,000- to 30,000-fold range of rates of shear can usually be covered. C. A. SLATER

1556. Apparatus for measuring surface tension at a liquid - liquid boundary. A. P. Grishin and Yu. I. Kozorezov (Groznenskiĭ Petroleum Inst.). *Zavod. Lab.*, 1955, **21** (7), 856–857.—The apparatus is based on the principle of measuring the max. pressure in a drop. Two capillary tubes of internal diameter 1 to 2 mm, one with a cone the other with a socket connection, are joined to the bottoms of two cylindrical vessels 4 to 5 cm in diameter. The orifice of the cone has a radius of 0·05 to 0·08 mm. The vessel carrying the capillary with the socket contains a liquid that wets glass better than the liquid in the other vessel. The liquid boundary is brought to a mark on the cylindrical part of the tube near the cone of the capillary that ends in the cone, and the pressure is read on a manometer. The pressure on one of the vessels is then altered

until a drop of liquid breaks off from the cone. The interfacial surface tension is calculated from the pressure readings. G. S. SMITH

1557. Determination of pore volume of solid catalysts. H. A. Benesi, R. U. Bonnar and C. F. Lee (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1963–1965.—The micro-pore vol. of solid catalysts and similar porous solids can be measured at 20° to 25° C by weighing the CCl_4 adsorbed by the dry sample (1 to 2 g) after equilibration for $\simeq 4$ to 16 hr. with a soln. in which the v.p. of the CCl_4 has been lowered to $\simeq 95$ per cent. of the saturation pressure by addition of *n*-hexadecane. This prevents interparticle condensation, with subsequent high values of pore vol. The accuracy is $\simeq \pm 0·01$ ml and the precision $> \pm 0·003$ ml per g; although the pore vol. are slightly lower than those obtained by nitrogen adsorption at $-196°$ C, the method is considered just as reliable for practical purposes and is much more convenient. W. J. BAKER

Optical

1558. Industrial spectrograph for direct measurement. H. Bückert (Optica S.p.A., Milan, Italy). *Metall*, 1954, **8** (23–24), 940–945.—The fundamental principles involved in the design of a new direct-reading spectrophotometer (illustrated) are discussed, and the limitations of the instrument are considered. The spectrograph is applicable to the rapid quant. determination of higher metal contents and is particularly useful when several different materials have to be analysed. J. P. STERN

1559. Investigations concerning light sources for spectrum analysis. IV. High-voltage spark-source with electronic control and its electrical characteristics. Á. Bardócz (Hung. Acad. Sci., Centr. Res. Inst. for Physics, Budapest). *Spectrochim. Acta*, 1955, **7** (5), 307–320.—Electrically reproducible high-voltage spark discharges across the analytical gap are controlled by means of a control gap or gaps. These are in turn regulated in time of breakdown by means of a thyratron, which is rendered conducting at desired intervals, varying between 50 and $50 \times 1/16$ sparks per sec., by supplying a positive grid-potential from a pulse generator. The circuit is arranged so that the excitation energy does not pass through the thyratron. The circuit may be modified to give 100 rectified discharges per sec. from a 50 c.p.s. supply by the inclusion of suitable diodes and to supply weak triggering discharges by means of a Tesla transformer. Full treatment of the effect of parameter variations on the electrical characteristics is given. P. T. BEALE

1560. The fifty-cycle arc in spectrochemical analyses. Oscillographic considerations with their implications in quantitative trace analysis. H. Gantzckow (Siemens-Schuckertwerke, Berlin, Germany). *Metall*, 1954, **8** (13–14), 528–531.—Oscillographic measurements on the 50-cycle arc show that the usual conditions of use, with ignition of the arc at the max. of each half-wave, do not result in optimum sensitivity. Maximum sensitivity is attained only when ignition is re-timed so that the max. area of each half-wave is utilised. Moreover, the regularities previously established for different high- and low-voltage sparks apply also for the

50-cycle arc and pulsating d.c. sparks. The increased sensitivity permits reduction of the exposure time by more than half. The special conditions attaching to carbon electrodes, and the causes of instability of the arc are discussed. The determination of lead and tin in copper is given as an example of the application of the method.   J. P. STERN

1561. Spectrographic analysis of powdered materials by introducing the powders into the discharge zone by means of a stream of air. A. K. Rusanov and T. I. Tarasova (All-Union Sci. Res. Inst. of Mineral Raw Materials, Moscow). *Zh. Anal. Khim.*, 1955, **10** (5), 267–275.—To improve the reproducibility of the arc method of spectrographic analysis it is necessary to ensure that the rate of evaporation of material into the discharge zone is made more constant and to stabilise the position of the flame in relation to the electrodes. Apparatus to fulfil these conditions is described. The material, as powder, is pulled from an agitated funnel through the arc by means of an air-extractor fan.
G. S. SMITH

1562. Measurement of solid samples on the Cary spectrophotometer. G. M. Wyman (Quartermaster Research Centre, Natick, Mass., U.S.A.). *J. Opt. Soc. Amer.*, 1955, **45** (11), 965–966.—A simple adapter is described which will hold solid samples, in the form of KBr discs, in the cell compartment of a Cary spectrophotometer. This has been found useful for measuring the absorption spectra of insoluble dyes and pigments in the ultra-violet and visible regions.   B. S. COOPER

1563. Improvements in or relating to apparatus for the determination of alloy constituents of metallic materials by spectrum analysis. VEB Fahrradwerk Elite-Diamant. Brit. Pat. 741,917; Date Appl. 4.12.53.—A portable apparatus for the non-destructive, spectro-analytical determination of the alloy constituents of any metallic surface is described. The complete assemblage is small and consists of an optical system and a spark-producing system; the latter is operated by an electromagnetic vibrator fed with a.c. current at $\simeq 42$ V from a mains transformer. When the apparatus is placed, by means of a one-point contact, on the metal to be examined, electrical contact is made between the outer support and the inner tungsten electrode, which can be adjusted so that its spring-loading device makes and breaks contact with the metal at each half-cycle of current. The light from the spark produced on breaking contact with the metal is viewed through a system consisting of an achromatic lens and a dispersing prism, and two telescopic lenses. A rotating eye-piece serves to focus the spectrum and a lateral adjusting screw enables all the spectrum lines to be viewed. It is claimed that, with experience of the line intensities, semi-quant. interpretation is possible and that the lower limits of detection are Cr 0·2, Mn 0·15, Mo 0·1, Ni 1, V 0·1, Co 3 and Ti 0·3 per cent., whilst the actual testing time occupies only a few minutes.   D. G. HIGGS

1564. Assignment of wavelengths on spectra recorded with Beckman model DK-1 spectrophotometer. S. Z. Lewin and R. H. Fairbanks (New York Univ., New York, U.S.A.). *Anal. Chem.*, 1955, **27** (12), 2020.—A very rapid and convenient technique, as accurate as the direct use of the monochromator scale, consists in transferring the wavelength scroll markings of the monochromator to a

sheet of transparent plastic (12 in. $\times$ 28 in. $\times$ 0·25 in.), which thereafter serves as the wavelength standard. When placed directly over the spectra under examination, and aligned correctly by reference marks, the wavelength of the absorption peaks can be measured accurately; this is of particular advantage when comparisons of wavelengths of absorption for different specimens are run on the same instruments. Details are given for the preparation of the standard, the size of which is suitable for the range 8 to 28 μ at speed 10. It is recommended that the calibration of the plastic standard should be against the absorption spectra of H_2O or of $CHCl_3$.   D. G. HIGGS

1565. Integrating sphere for the measurement of reflectance with the Beckman model DR recording spectrophotometer. J. A. Jacquez, W. McKeehan, J. Huss, J. M. Dimitroff and H. F. Kuppenheim (Army Med. Res. Lab., Fort Knox, Kentucky, U.S.A.). *J. Opt. Soc. Amer.*, 1955, **45** (11), 971–975. —The design of integrating sphere described requires a minimum of changes in the basic Beckman DR spectrophotometer so that the instrument is readily reconverted to the arrangement for transmission measurements. The sphere is $\simeq 4$ in. in internal diam. and was machined as two hemispheres from aluminium, the internal reflecting coating being MgO. With this accessory, spectral reflection curves may be recorded over the range 1000 mμ to 235 mμ.   B. S. COOPER

1566. A simple flame-photometer of high sensitivity. G. Gergely and P. F. Váradi (Res. Inst. Telecomm., Budapest). *Acta Phys. Acad. Sci. Hung.*, 1955, **5** (1), 51–64.—This is an English version of the paper published in *Magyar Kém. Foly.*, 1955, **61**, 182. (See *Anal. Abstr.*, 1956, **3**, 606.)   D. G. HIGGS

1567. Collaborative study of the performance of Cary spectrophotometers. J. M. Vandenbelt and C. H. Spurlock (Parke Davis & Co., Detroit, Michigan, U.S.A.). *J. Opt. Soc. Amer.*, 1955, **45** (11), 967–970.—Measurements have been made, at nine wavelengths in the range 230 mμ to 390 mμ, on standard alkaline solutions of K_2CrO_4, with 13 Cary spectrophotometers in different pharmaceutical laboratories. The values obtained are generally in good agreement, particularly in the central portion of the absorbance scale. Reproducibility on duplicate runs with the same instrument was usually better than the agreement between instruments.
B. S. COOPER

1568. Measurement of nearby stray radiation in ultra-violet spectrophotometers. D. D. Tunnicliff (Shell Development Co., Emeryville, Calif., U.S.A.). *J. Opt. Soc. Amer.*, 1955, **45** (11), 963–965.—In ultra-violet monochromators, the amount of stray radiation of wavelength close to that of the dispersed radiation may be estimated from the transmission of the very narrow 2537-A absorption peak of saturated mercury vapour. Nearby stray radiation is of particular importance when recording the very sharp absorption spectra observed at low temperatures, or the spectra of vapours.   B. S. COOPER

1569. New krypton light source for the vacuum ultra-violet. P. G. Wilkinson (Physics Dept., Univ. of Chicago, U.S.A.). *J. Opt. Soc. Amer.*, 1955, **45** (12), 1044–1046.—A krypton discharge lamp, similar in construction to the xenon lamp previously described (*Anal. Abstr.*, 1955, **2**, 2915),

has now been developed. This also is excited by microwave power at 2450 Mc. per sec. The useful spectral range is 165 to 125 mμ. B. S. COOPER

1570. Rotating step-sector for use with a.c. or other intermittent spectrographic light sources. R. N. Kniseley and V. A. Fassel (Iowa State College, U.S.A.). *J. Opt. Soc. Amer.*, 1955, **45** (12), 1032–1034.—The use of the rotating step-sector method for calibrating photographic emulsions for use in spectrographic analysis may lead to appreciable error with intermittent light sources owing to partial synchronisation. A design of step-sector is described which eliminates the risk of errors of this type. The sector consists of a series of stepped apertures spaced randomly about the periphery of the disc. B. S. COOPER

1571. Convenient technique for obtaining the ultra-violet and visible spectra of pure liquids. B. M. Mitzner (Columbia University, N.Y., U.S.A.). *J. Opt. Soc. Amer.*, 1955, **45** (11), 997–998.—Absorption cells of short path-length and with sodium chloride windows, as commonly used for infra-red absorption studies, are also suitable for the visible and ultra-violet regions; 0·1 mm, 0·05 mm and 0·025 mm are suitable path-lengths for pure liquid samples. It is advisable to obtain a spectrum base-line with a non-absorbing liquid in the cell in order to minimise scattering effects. B. S. COOPER

1572. Some observations regarding photometric reproducibility between ultra-violet spectrophotometers. L. Cahn (Beckman Instruments, Fullerton, Calif., U.S.A.). *J. Opt. Soc. Amer.*, 1955, **45** (11), 953–957.—The results of several recent collaborative studies of spectrophotometer performance are reviewed. Contributions to the total error of sample preparation error, wavelength error, 100 per cent. line error and linearity error are discussed. Results for two hitherto unpublished experiments on Beckman DU spectrophotometers are included. B. S. COOPER

1573. Automatic ultra-violet spectral scanning of chromatographic effluents. W. C. Kenyon, J. E. McCarley, E. G. Boucher, A. E. Robinson and A. K. Wiebe (Hercules Powder Co., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1888–1895.—An attachment to a Cary spectrophotometer is described with which the u.v. absorption spectrum can be obtained automatically on each of 200 or more chromatographic eluates. The record, over a 16-hr. period (overnight), gives a quant. and qual. determination of the components in the mixture. Gradient elution is employed to increase the versatility of the technique. The scanning of the u.v. spectrum over the range 400 to 200 mμ is controlled by the volume of eluate collected and not by the flow rate, which is more difficult to control. The eluate from the column is passed into a container, operated by a pair of solenoid valves in conjunction with a photo-electric detector, which splits the eluate into equal volumes, automatically scans the absorption spectrum and finally passes the eluate to a collecting rack in the same order as the recorded spectrum. As many as 20 different compounds have been detected in one sample by the apparatus. A quant. analysis is given for a synthetic mixture of benzene, anisole, benzaldehyde, acetophenone, phenol, benzoic acid and benzyl alcohol; the degree of recovery is within ±3 per cent. of the amount added. D. G. HIGGS

1574. Device for automatic measurement of integrated absorption. V. Z. Williams, V. J. Coates and F. Gaarde (Perkin - Elmer Corp., Norwalk, Conn., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 2017–2018.—An attachment to the Perkin - Elmer model 21 spectrophotometer has been developed which will integrate the absorbance value continuously as the spectrum is being recorded and present the integrated value on a counter. A pen system is attached so that, on the abscissa border of the spectrum unit, integrated values are marked by dashes; this enables fairly accurate absolute intensity values to be read directly from the spectrum. The device is applicable to both linear wavelength and linear wave-number instruments. Reproducibility is good and the accuracy is within 1 per cent. D. G. HIGGS

1575. Infra-red capillary cell for volatile liquids. R. H. Pierson and A. L. Olsen (U.S. Naval Ordnance Test Sta., China Lake, Calif., U.S.A.). *Anal. Chem.*, 1955, **27** (12), 2022.—Two simple modifications are described to overcome the volatilisation difficulties when the capillary technique is used on volatile solutions in i.r. analysis. (*i*) A slight depression is made with a drill or burring tool, 3/16 in. × 5/32 in., into the top of the assembled rock-salt cell, such that, when filled with the solvent under examination, gravity feed ensures that the capillary is always full of solvent. (*ii*) For highly volatile solvents, *e.g.*, CS_2 or acetone, a Teflon or polyethylene plug with a tapered end is made to fit into the depression as in (*i*), and into this is inserted a glass delivery-tube, which is maintained full, and replenished if necessary during the spectrum run. Even modification (*ii*) is not suitable for diethyl ether or other liquids of b.p. <40° C. D. G. HIGGS

1576. Determination of refractive indices and specific optical dispersions of opaque or intensely coloured substances with the Brewster refractometer. M. Palumbo (Central Chem. Lab., Dogane e I.I., Rome). *Olii Min.*, 1955, **32** (9), 191–193.—A chiefly theoretical account of the Brewster refractometer is given, with a description of the apparatus, which is compared with the Pulfrich and Abbé types. C. A. FINCH

Thermal

1577. A semi-micro hot-plate with sensitive distillation control. J. T. Stock and M. A. Fill (Norwood Tech. Coll., London, England). *Lab. Practice*, 1955, **4** (12), 501–502.—Details of construction are given, and assemblies for benchtop use, for tilting, and for use on a retort stand are described. O. M. WHITTON

1578. New use of a calorimetric bomb in quantitative chemical analysis. E. Przybylski. *Roczn. Państw. Zakł. Hig.*, 1954, **5** (2), 170; *Referativnyǐ Zh., Khim.*, 1955, Abstr. No. 11,907.—Ignition of $\simeq 1$ g of sample in O, at 35 to 40 atm., in a calorimetric bomb is used for determining metals in food, etc. With materials difficult to burn, lactose is added. The sample is made into a tablet and combustion is started with a piece of cotton heated with a platinum wire. The content of metals in the ash is determined polarographically. Examples of the determination of Zn in rubber and Cu in mushrooms are given. G. S. SMITH

1579. Modern combustion furnaces for organic elementary analysis. W. Zimmermann. *Chem. Tech., Berlin*, 1955, **7** (10), 595–598.—A discussion is given of the modern apparatus for rapidly effecting the micro- and semi-micro elementary combustion analysis of organic compounds by the Pregl method for C and H, the Dumas - Pregl method for C and N, and the Unterzaucher method for O. Descriptions are given of typical forms of (commercial) apparatus in which the heating of the combustion tube is effected rapidly and evenly and is automatically controlled to within fine limits.

H. L. WHITEHEAD

1580. High-vacuum filament furnace for gas analysis of metals. G. A. Consolazio and W. J. McMahon (Ordnance Corps, Watertown Arsenal Lab., Watertown, Mass., U.S.A.). *Science*, 1955, **122**, 764–765.—A special design of high-vacuum filament furnace is described that enables the gases evolved from metals to be transferred directly to a conventional type of mass spectrometer for analysis.

H. F. W. KIRKPATRICK

Electrical

1581. Continuous paper-electrophoresis apparatus. B. Mondovi and E. Antonini (Biol. Chem. Inst., Univ., Rome). *Ric. Sci.*, 1955, **25** (9), 2631–2635.—A simple and inexpensive apparatus for continuous paper electrophoresis is described. The apparatus, which has graphite electrodes, is illustrated, together with the electrical circuits used, and the method of operation is given in detail. The characteristics of some filter-papers are described.   C. A. FINCH

1582. Electrophoresis in agar plates. A. Bussard and D. Perrin (Inst. Pasteur, Paris, France). *J. Lab. Clin. Med.*, 1955, **46** (5), 689–701.—A simple agar-plate electrophoresis technique is described and details for the construction of the necessary apparatus are given. Conditions affecting the separations obtained and the behaviour of both charged and uncharged particles are investigated. The use of the method for serum analysis is described and the advantages over electrophoresis on paper are discussed.   W. H. C. SHAW

1583. Continuous polarographic analysis. I. The dropping-mercury electrode as reference electrode. J. V. A. Novák (Polarographic Inst., Acad. Sci., Prague, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1955, **20** (5), 1076–1089.—The conventional calomel or mercury-pool electrodes are not suitable as reference electrodes for continuous polarography, *e.g.*, in automatic process control, because they quickly become polarised. Under certain conditions the dropping electrode can be used as a reference electrode and two such systems are described. When the soln. to be polarographed contains a depolariser in sufficient concn., both the dropping-mercury electrodes (anode and cathode) can dip into the same soln.; the reference electrode then remains almost unpolarised. The second system, in which the two dropping-mercury electrodes dip into soln. of different composition, is more suitable for electrolysis of soln. containing redox systems or strong oxidising agents which are reduced at high positive potentials, such as soln. of $Fe^{\cdots}$ in dil. HNO_3, or for systems in which electrolysis results in insoluble products. The determination of $Ti^{\cdots}$ and $Fe^{\cdots}$, during the automatic control of a process for the preparation of TiO_2, in the presence of a large excess of $Ti^{\cdots\cdots}$ and $Fe^{\cdots}$, is given as an example, either electrode system being suitable. It was also found possible to determine continuously the concn. of CO in the atmosphere. The CO is passed over heated I_2O_5, the liberated I is oxidised by alkaline hypobromite to iodate, which is determined polarographically. The method is suitable for the determination of CO in concn. of 0·01 to 0·0001 per cent. by vol.

II. Reference electrodes with soluble reaction products. J. V. A. Novák. *Ibid.*, 1955, **20** (5), 1090–1095.—The behaviour of a number of electrodes is studied when these dip into soln. of such composition that the products formed as a result of electrolysis are soluble and easily carried away from the vicinity of the electrodes. The potential of the platinum electrode in a flowing soln. containing $Fe^{\cdots}$ and $Fe^{\cdots}$ is dependent on the current at low current densities to the same extent as is the calomel electrode, but is still independent of time at current densities which would polarise this electrode. For the continuous analysis of cyanide soln. a platinum reference electrode can be used in the presence of nitro compounds as depolarisers.

P. S. STROSS

1584. Treatment of polarographic data by the method of least squares. II. Simultaneous estimation of the diffusion current and the half-wave potential. V. B. Vouk, P. K. Karmalkar and O. A. Weber (Inst. Med. Res., Yugoslav Acad. Sci., Zagreb, Yugoslavia). *Arhiv Kem.*, 1955, **27** (1), 9–13.—The method of least squares has been applied to the simultaneous determination of $E_{\frac{1}{2}}$ and i_d with an accuracy slightly greater than that obtained from the usual graphical methods. The method is very well suited to the analysis of composite current-voltage curves, particularly for those metals whose curves tend to coalesce, *e.g.*, those of $Pb^{\cdots}$ and $Tl^{\cdots}$. The paper is mainly mathematical in its treatment, but the equations derived are illustrated by use of the data collected from the polarograms of $4·0 \times 10^{-4} N$ $TlNO_3$ and $4·0 \times 10^{-4} N$ Pb acetate in $0·1 N$ KCl as supporting electrolyte.   D. G. HIGGS

1585. Improvements in or relating to polarographs. Tinsley (Industrial Instruments) Ltd. (N. Circular Rd., London). Brit. Pat. 740,486; Date Appl. 18.5.53.—The diffusion current (i_d) flowing through the cell can be switched directly to the galvanometer and thence on to give the normal i_d trace on a moving-coil type of pen-recorder, or to a resistor in parallel with a large capacity condenser. Owing to the time-lag of the latter, the derivative is that of the mean value of the electrolytic current and not the derivative of the rise and fall of the i_d. Activation of the photocell allows current to flow in the grid of a gas-filled thermionic valve which, in turn, draws current in the anode circuit from a separate transformer winding. The d.c. in the anode circuit is smoothed by a choke and a condenser before passing on to drive the pen-recorder. Also connected to the anode circuit is a feedback network, in parallel with the galvanometer; a current proportional to the feedback voltage flows through the galvanometer in opposition to the current which is proportional to the derivative of the i_d. The overall effect on the galvanometer of these opposing currents is to maintain the light beam in such a position that the recorder records only the first derivative of the mean i_d.   D. G. HIGGS

1586. An apparatus for rapid oscillographic quantitative analysis. P. Valenta and J. Vogel (Polarographický Ústav, Akad. Věd, Prague, Czechoslovakia). *Chem. Listy*, 1955, **49** (3), 361–366.—The construction of a relatively simple adapter for the cathode-ray oscilloscope Křižík N-522 is described; it is designed to replace the complicated apparatus hitherto required for the saw-tooth-voltage impulse method of oscillographic quantitative polarography. The device makes possible a determination of the depolarisator by measuring the height of the max. of the appropriate curve *i* vs. *E*, as well as a titrimetric determination by comparing the curves *i* vs. *E* of the test soln. with those of a soln. of known concn.

G. GLASER

1587. Electrometric titrations with two polarised second-order electrodes. S. Samson (Inst. Soil Research T.N.O., Groningen, The Netherlands). *Anal. Chim. Acta*, 1955, **13** (5), 473–486.—The possibility of making electrometric titrations at const. resistance with two polarised second-order electrodes (*i.e.*, reversible with respect to both components of the reaction) is discussed fully. The polarisation curve of the Ag - AgCl electrode has been studied theoretically and experimentally to find the best conditions for chloride titrations. The prep. and handling of electrodes for making quick titrations with 0·005 N AgNO₃, the titration apparatus used, and some practical applications are described.   W. J. BAKER

1588. A high-frequency titration apparatus. J. C. Clayton, J. F. Hazel, W. M. McNabb and G. L. Schnable (Univ. Pennsylvania, Philadelphia, Pa., U.S.A.). *Anal. Chim. Acta*, 1955, **13** (5), 487–493.— The high-frequency titrimeter described and illustrated is a modification of Hall's apparatus (*Anal. Chem.*, 1952, **24**, 1244), and responds to either effective capacitance or effective conductance changes in the titration-cell circuit. Changes in effective capacity are measured by adjusting a variable capacitor to reproduce a certain grid-bias voltage, whilst changes in effective conductance are determined from changes in the grid-bias of the oscillator tube as indicated approx. by the electron-ray tube and measured by the external voltmeter. The end-point is determined from the linear plots in the region near the equivalence point. Typical titration curves obtained by each method are shown, and new methods of temp. control (including use of the electrodes themselves) are described.   W. J. BAKER

1589. Some applications of high-frequency titrimetry. J. P. Young (Indiana Univ., U.S.A.). *Dissert. Abstr.*, 1955, **15** (8), 1302–1303.—Oscillometry can be used for the volumetric determination of lithium halides, NaSCN, NaI, KSCN and potassium tri-iodomercurate, etc., by titration with AgNO₃ in pyridine solution. The determinations of sodium salts are improved by using pyridine containing 30 per cent. of benzene as solvent. Mixtures of NaSCN and KSCN can be assayed accurately by titration with LiCl in pyridine solution. The presence of water decreases the accuracy of the determinations, particularly when using AgNO₃. Oscillometric and conductimetric methods can be used to determine alkali-metal acetates by titration with HClO₄ and H₂SO₄, in the presence or absence of HNO₃, and other acids and salts by titration with K acetate, both titrations being performed in glacial acetic acid solution. Sulphuric

acid acts as a monobasic acid in these titrations, and water must be limited to ≯0·5 per cent. w/w.

S. C. JOLLY

1590. Second-differential automatic titration. I. An automatic titrator, type AT-1, and the determination of the main source of titration error. Seishi Takagi and Yoshihiro Maekawa (Pharmaceutical Inst., Kyoto Univ., Japan). *Japan Analyst*, 1954, **3** (6), 478–481.—A new automatic titrator for potentiometric titrations, in which use is made of the marked change in the value of the second differential at the end-point, was constructed and studied. The change in voltage between the electrodes, which are inserted in the sample soln., is amplified and its first differential is obtained by the use of a high resistance and a condenser. The differential is amplified and the second differential is similarly obtained; the potential difference of the latter is again amplified and connected to a relay which regulates the stopper of the burette. Sources of error were examined and it was found that the effect of the rate of titration predominates.

II. An automatic titrator, type AT-11, and the effect of rate of titration on the error. Yoshihiro Maekawa. *Ibid.*, 1954, **3**, 482–484.—A new automatic titrator (AT-II) was constructed in which two alternating currents with a phase difference of 180° were used. For amplification and differentiation a system similar to that of AT-I was used. This apparatus enables the rate of titration to be decreased near the end-point, where the change in voltage becomes more marked. Results of potentiometric titration of iodine with 0·1 N Na₂S₂O₃ were statistically analysed and it was again confirmed that a higher rate of titration vitiates both accuracy and reproducibility.

III. Characteristics of electric differential circuit by using Heaviside's operational calculus. *Ibid.*, 1954, **3**, 484–488.—The characteristics of the instruments described above were examined by the use of Heaviside's operational calculus with the equivalent circuits. It was found that the best second-differential voltage is obtained when the time constants of each differential circuit are the same. The main source of error appears to be due to the slow response of the circuit for the second differentiation.

IV. An automatic titrator, type AT-111, and errors of some potentiometric titrations. *Ibid.*, 1954, **3**, 488–493.—The electronic circuit of AT-II was modified according to the result obtained in Part III. Examination of the output current was carried out to eliminate possible sources of error. Several potentiometric redox titrations were made and the results statistically analysed. Iodimetric titration with standard Na₂S₂O₃ soln., with a platinum electrode, was satisfactory, the error being −0·03 to +0·33 per cent. for 0·1 N soln. (rate of titration, 10 ml per 5 min.), +0·05 to +0·37 per cent. for 0·01 N soln. (20 ml per 10 min.), and 0 to 2·5 per cent. for 0·001 N soln. (20 ml per 3 min.).   K. SAITO

1591. The adsorption micro-electrode as an indicator of halogens in the atmosphere. B. Kamienski and J. Kulawik (Polish Acad. Sci., Warsaw). *Bull. Acad. Polon. Sci. III*, 1955, **3** (7), 401–406.— An adsorption micro-electrode of the type described by Kamienski (*Bull. Acad. Polon. Sci.*, 1948, 128; 1949, 75; 157; 171; 1951, 199) is found to be very sensitive to traces of halogens in the atmosphere. They increase the potential of the micro-electrode in a positive direction. Concentrations of 0·00001

per cent. change the potential appreciably. The action of the halogens diminishes with a decrease in the oxidation potential. Reducing agents, such as carbon monoxide, hydrogen, hydrogen sulphide and acetylene, change the potential in a negative direction.   R. J. MAGEE

1592. Analyses of gaseous and liquid mixtures with the mass spectrometer MS-1. V. L. Tal'roze, G. D. Tantsȳrev and Ya. A. Yukhvidin (Inst. Chem. Phys. Acad. Sci. USSR). *Zavod. Lab.*, 1955, **21** (10), 1174–1182.—The use of a mass spectrometer for analysing mixtures of acetylene, ethylene, ethane and propane with argon as internal standard, mixtures of heptane, *cyclo*hexane, 2:2:3-trimethyl-pentane and *n*-decane with benzene as internal standard, and mixtures of *n*-butanol, ethanol, methanol, acetone and methyl acetate with benzene as internal standard, is described. G. S. SMITH

1593. Improvements in gas analysing apparatus. National Coal Board (London). Brit. Pat. 731,801; Date Appl. 10.10.52.—The apparatus described consists of two electrically heated wires forming the two opposite arms of a Wheatstone bridge, one contained co-axially in a support tube <4 mm in diameter, in which heat loss is effected by conduction, whilst in the second, contained co-axially in a support tube >4 mm in diameter, the heat loss is due to turbulence, and is almost entirely effected by convection. The other two arms of the bridge are formed by a potentiometer and a source of e.m.f.; the two filaments are mutually joined to the potentiometer via a galvanometer. Both filaments are horizontally positioned in metal containers, joined by means of a pipe at the base, so that the gas under examination flows downwards around one filament and upwards around the other. The apparatus is adjusted to zero deflection by using air or another gaseous mixture, and the relative change in resistance of the two filaments is measured when the gas under examination is circulated through the apparatus. It is claimed that CO_2 in water vapour $+ CH_4$, or water vapour $+ CO$ (producer gas), or water vapour $+ H$ (water gas), or $CO + NO$ (boiler-flue gases) can readily be determined and that, once calibrated, the galvanometer scale can be read directly in terms of percentage CO_2 in any of the gaseous mixtures.

                                      D. G. HIGGS

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use in the text of an abbreviation or symbol the word is printed in full.

alternating current	.	a.c.	millicurie	.	.	.	.	mC
ampere	.	amp.	milligram	.	.	.	.	mg
Ångstrom unit	.	A	millilitre	.	.	.	.	ml
anhydrous	.	anhyd.	millimetre	.	.	.	.	mm
approximate, -ly	.	approx.	millimicron	.	.	.	.	$m\mu$
aqueous	.	aq.	millivolt	.	.	.	.	mV
atmospher, -e, -ic	.	atm.	minimum	.	.	.	.	min.
boiling-point	.	b.p.	minute (time)	.	.	.	.	min.
British thermal unit	.	B.Th.U.	molar (concentration)	.	.	.	M
calorie (large)	.	kg-cal.	molecul -e, -ar	.	.	.	mol.
calorie (small)	.	g-cal.	normal (concentration)	.	.	.	N
centimetre	.	cm	number	.	.	.	.	no.
coefficient	.	coeff.	observed	.	.	.	.	(obs.)
concentrated	.	conc.	ounce	.	.	.	.	oz
concentration	.	concn.	part	.	.	.	.	pt.
critical	.	crit.	patent	.	.	.	.	pat.
crystalline	.	} cryst.	parts per million	.	.	.	p.p.m.
crystallised	.		per cent. wt. in wt.	.	.	per cent. w/w
cubic	.	cu.	per cent. wt. in vol.	.	.	per cent. w/v
current density	.	c.d.	per cent. vol. in vol.	.	.	per cent. v/v
cycles per second	.	c.p.s.	potential difference	.	.	.	p.d.
decompos -ing, -ition	.	(decomp.)	pound	.	.	.	.	lb
density	.	ρ	precipitate	.	.	.	.	ppt.
density, relative	.	d or wt. per ml	precipitated	.	.	.	pptd.
derivative	.	deriv.	precipitating	.	.	.	pptg.
dilute	.	dil.	precipitation	.	.	.	pptn.
direct current	.	d.c.	preparation	.	.	.	prep.
distilled	.	dist.	qualitative, -ly	.	.	.	qual.
electromotive force	.	e.m.f.	quantitative, -ly	.	.	.	quant.
electron-volt	.	eV	recrystallised	.	.	.	recryst.
equivalent	.	equiv.	refractive index	.	.	.	n
experiment	.	expt.	relative humidity	.	.	.	R.H.
foot, feet	.	ft.	revolutions per minute	.	.	r.p.m.
gram	.	g	saponification value	.	.	sap. val.
gram-molecule	.	mole	saturated calomel electrode	.	S.C.E.
half-wave potential	.	$E_{\frac{1}{2}}$	second (time)	.	.	.	sec.
horse-power	.	h.p.	soluble	.	.	.	.	sol.
hour	.	hr.	solution	.	.	.	.	soln.
hydrogen ion concentration	[H·]	specific gravity	.	.	.	sp. gr.
hydrogen ion exponent	pH	specific rotation	.	.	.	$[\alpha]_{\lambda}$
inch	.	in.	square centimetre	.	.	.	sq. cm
infra-red	.	i.r.	standard temperature and	
insoluble	.	insol.	pressure	.	.	.	.	s.t.p.
kilogram	.	kg	temperature	.	.	.	.	temp.
kilovolt	.	kV	ultra-violet	.	.	.	.	u.v.
kilowatt	.	kW	vapour density	.	.	.	v.d.
maxim -um, -a	.	max.	vapour pressure	.	.	.	v.p.
melting-point	.	m.p.	volt	.	.	.	.	V
microcurie	.	μC	volume	.	.	.	.	vol.
microgram	.	μg	watt	.	.	.	.	W
microlitre	.	μl	wavelength	.	.	.	.	λ
micron	.	μ	weight	.	.	.	.	wt.
milliampere	.	mA						

In addition the following symbols are used—

greater than	.	.	$>$	less than	.	.	$<$
not greater than	.	$\not>$	not less than	.	.	$\not<$
is proportional to	.	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P., or D.A.B., together with the identifying numeral.

Radicles are represented by the usual symbols; positive ions have superscript dots and negative ions superscript dashes, e.g., Cu·, Al··, Cl', SO_4''. Metals that exist in more than one valency state are represented by their symbols with appropriate superscript roman numerals, e.g., ferric iron becomes Fe^{III} and cuprous copper Cu^I.

ANALYTICAL ABSTRACTS

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